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ELECTRON TRANSFER REACTIONS IN SOME
COBALT(II) - COBALT(III) SYSTEMS

A THESIS

Presented to
The Faculty of the Graduate Division

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ELECTRON TRANSFER REACTIONS IN SOME
COBALT(II) - COBALT(III) SYSTEMS

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PREFACE

This thesis was directed by Dr. Henry M. Neumann to whom I am indebted for his capable guidance. Also, I am indebted to Dr. H. R. Hunt, Jr. for keeping abreast of the problem and contributing several valuable suggestions. I wish to thank Dr. James A. Knight, Jr. and Messrs. C. Turner Lewis, Jr. and Robert J. Klett for courtesies extended to me at the Radio-isotopes Laboratory. In addition, I acknowledge the many friends and acquaintances too numerous to mention. I express my appreciation to the members of the reading committee, Dr. Erling Grovenstein, Jr. and Dr. H. R. Hunt, Jr. Especial thanks are due my wife for sacrifices made during this work.

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SUMMARY

The purpose of the present investigation was to study the kinetics of an oxidation-reduction system which is believed to occur by an outer sphere complex, and to determine factors which influence the rate. The system chosen for study contained cobalt(II) and cobalt(III) as central metal ions and 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, and 3,4,7,8-tetramethyl-1,10-phenanthroline as ligands. Cobalt(II) - cobalt(III) systems are known to have measurable rates as predicted by ligand field considerations. Studies, utilizing complexes differing widely in size, formal charge, and nature of ligand, indicate several different mechanisms are operative. The phenanthroline molecule is planar and cannot form bridges between two metal atoms, thus eliminating the possibility of an inner sphere complex. Substituted phenanthrolines differ in base strength and ligand field strength. Consequently, this system allows the study of the dependence of rate of electron transfer on ligand field strength without drastically altering the size or nature of the ligands.

The preparation of cobalt complexes containing substituted phenanthrolines has not been recorded in the literature. Tris-cobalt(II) and cobalt(III) complexes employing 5-nitro-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline were prepared and isolated as the perchlorates. The composition was confirmed by analyses. The perchlorate salts are soluble with difficulty but were converted to solutions by anion exchange with Dowex 1-X8 exchange resin. Also, the cobalt(II) complexes were prepared in situ.

Spectra of 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, and the corresponding tris-cobalt(II) and cobalt(III) complexes were determined in the region 200-1150 millimicrons. Spectra have been recorded for 1,10-phenanthroline and its compounds; however, a considerable portion of the reported spectra were found to be in error. No reports of spectra of the complexes of substituted phenanthrolines were found.

Spectra in the ultraviolet region are characterized by large molar absorbancy indices and are essentially the spectra of the ligands or slightly perturbed spectra due to complexation.

The cobalt(II) and cobalt(III) complexes do not possess isolated peaks in the visible region of the spectrum. The cobalt(III) complexes have shoulders which appear in the vicinity of 470 millimicrons which are capable of resolution. Resolved peaks possess molar absorbancy indices of 20 to 40.

The cobalt(II) complexes exhibit ligand field bands in the vicinity of 910 millimicrons with molar absorbancy indices less than ten. These bands are a direct measure of the ligand field strength and are ordered according to the base strengths of the ligands even though they differ only slightly in the wavelength of maximum absorption.

An unsuccessful attempt to resolve the tris(1,10-phenanthroline)-cobalt(III) ion into its enantiomorphous forms appears in the literature. This ion was successfully resolved employing antimonyl tartrate as resolving agent and using an ethanol-water mixture to decrease the solubility of the desired diastereoisomer. Also, the tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III) ion was partially resolved.

Optically active tris(1,10-phenanthroline)cobalt(III) ion was prepared by an asymmetric synthesis. Antimonyl tartrate preferentially converts the labile tris(1,10-phenanthroline)cobalt(II) ion into one diastereoisomer, which can be oxidized to the corresponding inert cobalt(III) complex. A product containing 74 percent of the dextrorotatory isomer was obtained in this manner.

Optical rotatory dispersion of levorotatory tris(1,10-phenanthroline)cobalt(III) perchlorate dihydrate was measured over the wavelength range 420-600 millimicrons. The optical rotatory curve is in agreement with an absorption peak in the vicinity of 470 millimicrons.

Magnetic susceptibilities of the tris-cobalt(II) complexes were determined at room temperature by the Gouy method. The values of magnetic moments are in the range 4.5 to 5.0 B.M. and indicate that the complexes are spin free.

The rate of electron transfer between tris(1,10-phenanthroline)cobalt(II) and tris(1,10-phenanthroline)cobalt(III) was measured by a radiochemical exchange technique employing cobalt-60, and also by the rate of racemization of optically active tris(1,10-phenanthroline)cobalt(III) ion as catalyzed by the labile tris(1,10-phenanthroline)cobalt(II) ion. A cursory investigation of exchange between cobalt(II) and cobalt(III) systems containing 5-nitro-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline was made employing radiochemical exchange and racemization techniques, respectively.

Homogeneous isotopic exchange reactions obey a simple relationship, the McKay equation, regardless of the mechanism of exchange. The relationship is:

$$\ln \left| \frac{A - A_{\infty}}{A_0 - A_{\infty}} \right| = - R \left(\frac{a + b}{ab} \right) t$$

where:

A = activity at time t

A₀ = activity at zero time

A_∞ = activity at infinite time

R = constant rate of exchange

t = time

a = concentration of one exchanging species

b = concentration of other exchanging species

Exchange between tris(1,10-phenanthroline)cobalt(II) and tris(1,10-phenanthroline)cobalt(III) was treated according to the McKay equation and plots of $\ln \left| \frac{A - A_{\infty}}{A_0 - A_{\infty}} \right|$ versus time were linear.

An attempt was made to fit the experimental data to a rate law of the form $R = k[a]^m[b]^n$ where k is the specific rate constant and m and n are the orders of the reaction in a and b, respectively. Analysis of the data according to the preceding rate law led to fractional orders. Also, values of k differed by a factor of two depending on the relative concentrations of cobalt(II) and cobalt(III).

Even though, from the purely empirical point of view, the data are fitted satisfactorily with non-integral orders, the mechanistic explanation of these values is obscure. The values of order are between zero and one, and suggest that a rate law of the following form may be operative:

$$R = k_1[\text{Co(II)}][\text{Co(III)}] + k_2[\text{Co(II)}] + k_3[\text{Co(III)}]$$

This rate law provided a fit of the data that was as satisfactory as the rate expression which contained fractional orders. Also, values of k in different concentration ranges did not deviate widely. The rate law with integral orders is thus believed to provide a more correct description of the system. Activation energy of the electron transfer was measured by the radiochemical technique in different ionic atmospheres.

The rate of electron transfer between the tris(1,10-phenanthroline)-cobalt(II) ion and the tris(1,10-phenanthroline)cobalt(III) ion was determined employing the change in optical rotation of the cobalt(III) complex as a measure of the rate of exchange. The data are fitted nicely by a bimolecular rate law. An activation energy of 5.8 kcal/mole and an entropy of activation of -35 cal/degree-mole were obtained in an ionic atmosphere of 0.10 M KNO_3 .

An insufficiency of data precluded a direct comparison of the rates of electron transfer of the systems under identical conditions. The data indicate that rates were ordered as follows: 5-nitro-1,10-phenanthroline < 1,10-phenanthroline < 3,4,7,8-tetramethyl-1,10-phenanthroline. The rates of exchange of 5-nitro-1,10-phenanthroline complexes and the 1,10-phenanthroline complexes differ by less than a factor of two but the rates of exchange of 1,10-phenanthroline complexes and 3,4,7,8-tetramethyl-1,10-phenanthroline complexes differ by a factor of eleven.

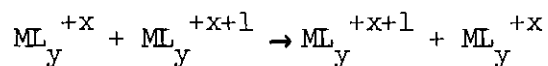
CHAPTER I

INTRODUCTION

Oxidation-reduction reactions have been utilized in various areas of chemistry for many years; however, this type of reaction has been studied from a mechanistic viewpoint for only a relatively short time. Oxidation-reduction reactions invariably are described in terms of a transfer of electrons from the reducing agent to the oxidizing agent. The purpose of mechanistic studies is to understand the way in which this transfer is accomplished. Studies of the redox reactions of complex ions which contain a transition metal as the central atom in the complex have provided the basis of much of our knowledge of this field.

A redox reaction between two ions of this type may proceed by one of two general mechanisms. In the first mechanism an atom or group is shared by the first coordination spheres of the central atoms at the time of the electron transfer. At one time this mechanism was known as the "atom transfer" mechanism, since the most positive evidence for it exists in those cases in which an atom originally bound to one of the reactant metals is found bound to the other metal in the products. At the present time, this mechanism is more frequently referred to as proceeding by a "bridged activated complex." In the second mechanism, a direct electron transfer occurs between complex ions whose first coordination spheres share no common group or atom. This mechanism is referred to either as the "electron transfer" mechanism or as involving an "outer sphere complex."

If the oxidizing agent and reducing agent differ in structure only by one electron, the oxidation-reduction reaction leads to no net chemical change and is called an exchange reaction. The reaction may be written generally as



where M is the central metal atom, and L is the attached ligand.

The purpose of the present research is to investigate a system of oxidation-reduction exchange reactions which are believed to proceed by the "electron transfer" mechanism, and attempt to determine factors which influence the rate of exchange. The system chosen for study contains cobalt(II) and cobalt(III) as central metal atoms. The metal and the particular oxidation states were selected because rates of exchange are known to be measurable with a variety of ligands. A review of the cobalt(II)-cobalt(III) systems which have appeared in the literature is now reported.

The system consisting of $Co(NH_3)_6^{+2}$ and $Co(NH_3)_6^{+3}$ has been studied by several investigators. McCallum and Hoshowsky¹ reported virtually no exchange, but more recent investigations indicate a slow but measurable exchange. Lewis, Coryell, and Irvine² examined the system and reported a large catalytic effect due to oxygen. They reported a bimolecular rate constant of less than $0.0023, M^{-1}hr^{-1}$ under the following conditions: pH = 10.7, $[Co(NH_3)_6^{+3}] = 0.0895 M$, concentration of cobaltous complexes = $0.089 M$ (60 percent in the form $Co(NH_3)_6^{+2}$), $[NH_3] = 5.7 M$, temperature = $45.1^\circ C$, ionic strength = 0.98. A zero time exchange of approximately eight percent was observed.

Biradar, Stranks, and Vaidya³ examined the system very carefully

and were able to eliminate the zero time exchange by the meticulous exclusion of oxygen. They reported a bimolecular rate constant of $3.96 \times 10^{-3} \text{ M}^{-1}\text{min}^{-1}$ under the following conditions: $\text{pH} = 9.46$, concentrations of cobaltous and cobaltic complexes varied between 1×10^{-2} and $8 \times 10^{-2} \text{ M}$, $[\text{NH}_3] = 5 \text{ M}$, ionic strength = 1.00, and a temperature of 64.5° C . The activation energy was determined to be $30.1 \pm 0.8 \text{ kcal/mole}$. An isotopic dilution technique was employed to determine the amount of various mixed hydroxoamine complexes of cobalt(III) in the products. These data were interpreted to indicate that exchange occurred through a hydroxo bridged intermediate formed by the $\text{Co}(\text{NH}_3)_6^{+3} \cdot \text{OH}^-$ ion pair and the various cobaltous complexes. The investigators reported a bimolecular rate constant of $0.34 \text{ M}^{-1}\text{min}^{-1}$ at 64.5° C for this process, and indicated that it may be in error by a factor of two due to approximations employed for its calculation. Also, the process was reported to have an activation energy of $12.9 \pm 1.0 \text{ kcal/mole}$ and an entropy of activation of $-35 \pm 5 \text{ cal/mole-degree}$. Stranks⁴ has examined the exchange in systems consisting of cobaltous amine complexes and mixed aquo or hydroxo complexes of cobalt(III). The rates increase and the entropy of activation becomes more positive as amine groups are replaced by aquo or hydroxo ligands.

The rate of exchange for the system tris(ethylenediamine)cobalt(II), tris(ethylenediamine)cobalt(III) has been studied by several investigators.^{2,5} Lewis et al.² studied the exchange by a radiochemical technique and their work was later verified by Dwyer and Sargeson⁵ employing the change of optical activity of the cobaltic complex as a measure of the rate of exchange. The latter examination gave a bimolecular rate constant of $0.77 \times 10^{-4} \text{ M}^{-1}\text{sec}^{-1}$, activation energy of $14.1 \pm 0.2 \text{ kcal/mole}$, entropy

of activation of -32 cal/mole-degree at 25° C and an ionic strength of 0.98 . These values are in agreement with those of Lewis et al. Dwyer and Sargeson report that the rate is independent of hydroxide ion concentration and observed no catalytic effect due to excess ethylenediamine or specific anion effects except the expected ionic strength dependence. A linear relationship exists between $\log k$ and the square root of the ionic strength. The investigators suggest that the above facts preclude hydrogen atom transfer involving the conjugate base forms of the complexes, as well as ethylenediamine or anion bridges. This system is usually considered to be a case of direct electron transfer; however, Stranks⁶ examined the system and reported that the rate was dependent on hydroxide ion concentration, and also observed a catalytic effect due to chloride ion. He has also replaced tris-(ethylenediamine)cobalt(III) by mixed ethylenediamine, aquo or hydroxo complexes and noted a progressively faster rate as substitution of ethylenediamine by aquo or hydroxo groups was increased.

Adamson and Vorres⁷ measured the rate of exchange between $\text{Co}(\text{EDTA})^{-2}$ and $\text{Co}(\text{EDTA})^{-1}$ by a radiochemical technique. Their results have been verified by Yong Ae Im and D. H. Busch,⁸ who employed the loss of optical activity of the cobaltic complex as the criterion for exchange. Adamson and Vorres reported a bimolecular rate constant of $0.75 \text{ M}^{-1}\text{hr}^{-1}$ at pH 2 and temperature of 85° C. They also reported an activation energy of 22 kcal/mole and an entropy of activation of -16.6 cal/mole-degree. Im and Busch stated that the bimolecular rate constant in D_2O was comparable to the constant when H_2O was employed as solvent. The rate of exchange is catalyzed by barium ions.

The rate of exchange of the $\text{Co}(\text{PDTA})^{-2}$, $\text{Co}(\text{PDTA})^{-1}$ system, where

PDTA is the abbreviation for propylenediaminetetracetic acid, has been studied by Im and Busch.⁹ The rate was measured by the change of optical activity and was found to be comparable to the corresponding ethylenediaminetetracetic acid system. At pH 2 an activation energy of 24 kcal/mole and entropy of activation of -9.3 cal/mole-degree were reported.

Exchange between $\text{Co}(\text{C}_2\text{O}_4)_3^{-4}$ and $\text{Co}(\text{C}_2\text{O}_4)_3^{-3}$ has been examined by two groups^{10,11} and the conclusion was that the majority of exchange occurred by a thermal reductive decomposition of the $\text{Co}(\text{C}_2\text{O}_4)_3^{-3}$ complex with only a rather insignificant portion proceeding by electron exchange. Dainton et al.¹⁰ indicate that the small amount of exchange that does occur does not proceed by the electron transfer mechanism but proceeds instead by an oxalato bridge supplied by detaching one end of a ligand of the cobaltic complex.

Exchange in the aquo complexes of Co(II) and Co(III) was studied in 1.0 F perchloric acid.¹² A bimolecular rate constant of $40 \text{ M}^{-1}\text{min}^{-1}$ was reported at 3.2° C, and an activation energy of 13.2 kcal/mole and entropy of activation of -13 entropy units were recorded. Specific anion effects were noted for nitrate and bisulfate as compared to perchlorate, and the rate in D_2O was only about one-half that found in water.

In attempting to study the exchange between the tris(1,10-phenanthroline)cobalt(III) ion and free phenanthroline, Ellis, Wilkins, and Williams¹³ observed a catalytic effect due to cobalt(II) impurity. They attributed this effect to the electron exchange reaction between the tris-(1,10-phenanthroline) complexes of cobalt(II) and cobalt(III) and, by studying the effect of added cobalt(II), obtained a specific rate constant of $268 \text{ M}^{-1}\text{min}^{-1}$ for the electron exchange reaction at 20° C. By the same

method, a constant of $1120 \text{ M}^{-1}\text{min}^{-1}$ was obtained at 45°C for exchange between the tris(2,2'-bipyridine) complexes.

Baker, Basolo, and Neumann¹⁴ extensively studied the electron transfer in the tris(1,10-phenanthroline)cobalt(II), tris(1,10-phenanthroline)-cobalt(III) system by a tracer technique. These investigators also reported a cursory examination of the corresponding systems employing 2,2'-bipyridine and 2,2',2''-tripyridine as ligands.

In the phenanthroline system an unusual anion dependency was found. The rate was larger by a factor of two to three when KNO_3 was employed to maintain a constant ionic atmosphere as compared to KCl . The rate at low chloride ion is slower than with no added chloride; however, additional chloride ion increases the rate. Also, the dependence of the rate on the concentration of cobalt(II) complex is stated to be one-half. In KNO_3 solution this dependency is approximately one. A "buried" ion pair formed between the cobalt(III) complex and the chloride ion was offered as a suggestion to explain the unusual results.

Bimolecular rate constants of about $1.1 \text{ M}^{-1}\text{sec}^{-1}$ with no added electrolyte and $5.5 \text{ M}^{-1}\text{sec}^{-1}$ at pH 8.29 in 0.10 M KNO_3 were recorded for the phenanthroline system at zero degrees centigrade. These are compared to approximate values of 2 and $12 \text{ M}^{-1}\text{sec}^{-1}$ for the 2,2'-bipyridine and 2,2',2''-tripyridine systems, respectively, at zero degrees centigrade. An activation energy of $17 \pm 5 \text{ kcal/mole}$ and an entropy of activation of +4 entropy units were reported for the phenanthroline system with no added electrolyte.

Recently two exchange systems which possess unusual geometries compared to the usual octahedral arrangement have been studied by a radio-

chemical tracer technique. Weiher, Katz, and Voigt¹⁵ studied the exchange between bis(cyclopentadienyl)cobalt(II) and the bis(cyclopentadienyl)cobalt(III) ion in anhydrous acetone. The exchange is reported to occur instantaneously. These workers also report that no exchange occurs between the bis(cyclopentadienyl)cobalt(III) ion and the aquated cobaltous ion in aqueous perchlorate solution.

Rasmussen and Brubaker¹⁶ examined the electron transfer between the 12-tungstocobaltate(II) and 12-tungstocobaltate(III) anions. The rate was found to be independent of acid concentration over the range 0.025 M to 0.80 M hydrogen ion at constant ionic strength. The rate was found to be greatly dependent on ionic strength. Also, a specific cation effect was noted for the potassium ion as compared to the lithium ion. The activation energy varies with ionic strength, and an extrapolated value of 18 kcal/mole is reported at zero ionic strength. A bimolecular rate constant of $0.34 \text{ M}^{-1}\text{sec}^{-1}$ was reported for an ionic strength of 0.05 (lithium chloride) at a temperature of 25° C. In this ionic atmosphere, an activation energy of $8 \pm 1 \text{ kcal/mole}$, and an entropy of activation of -35.4 ± 1 entropy units were recorded over the temperature range of 0 to 25° C.

Even though the cobalt(II), cobalt(III) systems reported in the literature were not conducted under identical conditions, a trend in the rate is evident. The spectrochemical series may be used to order the ligands according to increasing field strength: $\text{H}_2\text{O} < \text{C}_2\text{O}_4^{2-} < \text{EDTA} < \text{NH}_3 < \text{ethylenediamine} < \text{bipyridine} \approx \text{1,10-phenanthroline}$. When water is employed as ligand the reaction is fast. The rate is slower for ligands intermediate in the spectrochemical series, and increased rates are observed for the strong field ligands such as phenanthroline.

The general trend observed is in agreement with predictions employing ligand field theory. At low field strength, the cobalt(III) complex may achieve a spin-free state rather easily, and a fast reaction would be expected with the cobalt(II) complex, which, of course, is spin free. At high field strength, the cobalt(III) is spin paired and the cobalt(II) may be able to achieve a spin-paired state. The differences in bond dimensions and energy level spacings would be expected to be small and consequently, a rapid exchange would be expected. With an intermediate field strength, the cobalt(II) would probably be in a spin-free state and the cobalt(III) in a spin-paired state. Large differences in bond distances and energy level spacings would be expected, and a slow rate would be anticipated.

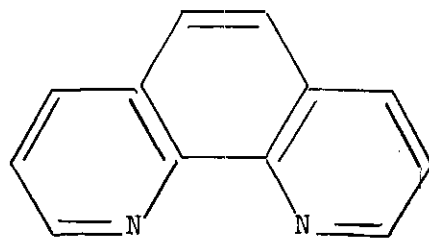
Data from the systems reviewed are tabulated in Table 1. Necessarily, one must point out that the systems may undergo exchange by different mechanisms and a direct comparison of rates, activation energies, and entropies of activation should be made with prudence.

In the present investigation, 1,10-phenanthroline or substituted phenanthrolines were chosen as ligands, since in such systems the oxidation-reduction reaction is believed to proceed by a direct electron transfer. Redox systems in which both oxidant and reductant are substitution inert prevent the formation of a bridged activated complex and are considered to take place by an outer sphere complex. In the present system, the cobalt(III) is substitution inert but the cobalt(II) complex is labile. The principal evidence of the inertness of the cobalt(III) complex is the slow exchange of the complex with C-14-labeled phenanthroline.¹³ The kinetic lability of the Co(II) complex has been demonstrated by rapid exchange both with C-14-labeled phenanthroline¹⁷ and with Co-60-labeled

Table 1. Exchange Data for the Cobalt(II)-Cobalt(III) System with Various Ligands

Ligand	Temperature ° C	k M ⁻¹ sec ⁻¹	Ionic Strength	Activation Energy	Entropy of Activation	Reference
Water	3.2	0.66	1.0	13.2	-13	12
EDTA	85	2.08×10^{-5}	1.0	22	-16.6	7
Ammonia	64.5	6.6×10^{-5}	1.0	30.1 ± 0.8		3
Ethylenediamine	25	7.7×10^{-5}	0.98	14.1 ± 0.2	-32	5
Bipyridine	0	2				14
Tripyridine	0	12				14
Phenanthroline	0	5.5	0.10 KNO ₃			14
Phenanthroline	0			17 ± 5	+ 4	14

cobaltous ion.¹⁸ Although an outer sphere mechanism cannot be unequivocally predicted when one of the complexes is labile, the geometry of the planar phenanthroline molecule¹⁹ makes the formation of a ligand bridge between metal ions extremely unlikely.



1,10-phenanthroline

Indirect evidence also supports this view. The labile complex, tris(2,2'-bipyridine)chromium(II) ion, has been utilized as the reducing agent for a series of cobalt(III) complexes of the general formula $\text{Co}(\text{NH}_3)_5\text{L}$, where $\text{L} = \text{NH}_3, \text{H}_2\text{O}, \text{OH}^-, \text{Cl}^-, \text{or Br}^-$.²⁰ This investigation reported that the only chromium(III) product was the tris(2,2'-bipyridine)-chromium(III) ion; however, other investigators report that the chromium(III) product is bis(2,2'-bipyridine)diaquochromium(III).²¹ Regardless of the above disagreement, the chromium(III) product apparently did not contain L in the cases of $\text{L} = \text{NH}_3, \text{Cl}^- \text{ or } \text{Br}^-$, a bridged activated complex probably did not exist, and the mechanism is considered to be of the outer sphere type. This is in contrast to the classical studies which employed aquated chromium(II) to demonstrate bridged activated complexes.²² The complexes of 2,2'-bipyridine and 1,10-phenanthroline are structurally similar, and the possibility of bridging by a ligand is certainly decreased in the case

of phenanthroline complexes as compared to bipyridine complexes. For these reasons it is believed that exchange occurs by an outer sphere mechanism, even though tris(1,10-phenanthroline)cobalt(II) is labile.

Since the complex $[\text{Co}(\text{phen})_3]^{2+}$ is labile, when its salts are dissolved in water there is rapid dissociation to give an equilibrium mixture containing Co^{2+} , $[\text{Co}(\text{phen})]^{2+}$, $[\text{Co}(\text{phen})_2]^{2+}$, $[\text{Co}(\text{phen})_3]^{2+}$, and phenanthroline. The equilibrium state is described in terms of the three equilibrium constants

$$K_1 = \frac{[\text{Co}(\text{phen})^{2+}]}{[\text{Co}^{2+}][\text{phen}]}$$

$$K_2 = \frac{[\text{Co}(\text{phen})_2^{2+}]}{[\text{Co}(\text{phen})^{2+}][\text{phen}]}$$

$$K_3 = \frac{[\text{Co}(\text{phen})_3^{2+}]}{[\text{Co}(\text{phen})_2^{2+}][\text{phen}]}$$

The following values have been reported in the literature for these constants.

Medium	$\log K_1$	$\log K_2$	$\log K_3$	Reference
0.1 M NaNO_3	7.31	----	----	23
0.1 M KCl	7.02	6.70	6.38	24
0.1 M KCl	6.96	6.73	6.08	25

Thus, although there is some uncertainty in the exact values of the constants, the order of magnitude is clearly established.

Although the step-wise equilibrium constants provide a complete

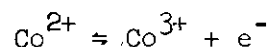
description of the equilibria it is useful to note the value of the overall equilibrium constant, K_{II} .

$$K_{II} = \frac{[\text{Co(phen)}_3^{2+}]}{[\text{Co}^{2+}][\text{phen}]^3} = K_1 K_2 K_3 \approx 10^{20}$$

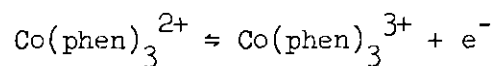
The corresponding constants for the cobalt(III) complexes have not been measured, but an indirect calculation of the overall constant

$$K_{III} = \frac{[\text{Co(phen)}_3^{3+}]}{[\text{Co}^{3+}][\text{phen}]^3}$$

is possible from electrode potential measurements. The potential for the



half-reaction²⁶ is -1.82 volts. The potential for the



half-reaction²⁷ is -0.40 volts. By use of these values and the Nernst equation²⁸ it can be shown that

$$K_{III} = 10^{24} \times K_{II}$$

Thus K_{III} has a value of about 10^{44} . Thus, for all practical purposes, the cobalt(III) possesses thermodynamic stability in addition to the kinetic inertness previously mentioned.

In addition to investigating the oxidation-reduction reaction of the phenanthroline complexes of cobalt(II) and cobalt(III), it was desirable to examine the behavior of the complexes containing substituted phenanthrolines as ligands. A variety of substituted phenanthrolines are available with widely differing base strengths^{29, 30} and presumably differing ligand field strengths. The 5-nitro and 3,4,7,8-tetramethyl derivatives were chosen since they provided a wide spread in base strengths.

Ligand	pK_{a}	Reference
unsubstituted	4.86	29
	4.96	30
5-nitro	3.57	30
3,4,7,8-tetramethyl	6.31	29

Thus, it was hoped that the effect of varying ligand field strength on the rate of exchange could be evaluated without changing greatly the size of the complexes, or altering extensively the nature of the ligands and complexes. The exchange reactions would be expected to proceed by the same mechanism.

CHAPTER II

EXPERIMENTAL

Chemicals

1,10-Phenanthroline was obtained from several suppliers and was recrystallized from water prior to use.

Substituted phenanthrolines were obtained from G. Frederick Smith Chemical Company. Several lots were purchased and the method of purification varied from time to time. They were used without purification unless otherwise specified.

The following chemicals were purchased as reagent grade and were utilized without further purification:

acetone

ammonium hydroxide

ammonium nitrate

ammonium thiocyanate

bromine

cobaltous chloride hexahydrate

cobaltous nitrate hexahydrate

calcium chloride

disodium ethylenediaminetetracetate dihydrate

ferric nitrate nonahydrate

magnesium perchlorate

potassium chloride

potassium nitrate
potassium hydroxide
silver nitrate
sodium chloride
sodium sulfate
sodium thiocyanate
sodium hydroxide
hydrochloric acid
nitric acid
sulfuric acid
perchloric acid

Sodium perchlorate was obtained from Columbia Organic Chemicals Co., Inc. and used without further treatment.

Potassium perchlorate was prepared by the neutralization of reagent grade perchloric acid with reagent grade potassium hydroxide. The salt was isolated and recrystallized from water.

Ethanol was either 95 percent or absolute and was utilized without treatment.

Methyl isobutyl ketone was obtained as reagent grade, and redistilled before using.

Dowex 1-X8 anion exchange resin was obtained in the chloride form and used without further treatment.

Chlorine was acquired from Tesco Chemical Company and used without further purification.

Potassium antimonyl tartrate was of undetermined quality, and was recrystallized from water prior to use.

Silver antimonyl tartrate was prepared by metathesis from potassium antimonyl tartrate and silver nitrate. The material is photosensitive and was prepared in small quantities as needed and protected from light.

Water for all reactions was distilled from acid dichromate and basic permanganate.

Radioactive cobalt-60 for tracer studies was obtained from Oak Ridge as a solution of cobaltous chloride in approximately 1.2 M hydrochloric acid. Treatment of this radioactive stock solution will be discussed in the appropriate sections.

Preparation of Compounds

Some of the cobalt phenanthroline complexes have been prepared by several methods. The compounds were prepared in small quantities as needed and a typical synthesis of each compound will be discussed. All analyses reported for C, H, and N were performed by Galbraith Laboratories, Knoxville, Tennessee.

Tris(1,10-phenanthroline)cobalt(II) Perchlorate

Aqueous Media. Twenty-five milliliters of 0.10 M CoCl_2 solution was slowly added to 3.0 grams of 1,10-phenanthroline which was partly dissolved in 75 ml of hot water. The CoCl_2 solution must be added to the phenanthroline solution, and must be added slowly with stirring to insure that sufficient phenanthroline is present in solution to completely complex the cobaltous ion in the tris form. The mole ratio of cobalt to phenanthroline was one to six. This precaution is necessary since the bis species is highly susceptible to air oxidation. The perchlorate salt was obtained by the addition of a dilute solution of sodium perchlorate. The compound

was collected on a medium porosity sintered glass filter, washed several times with water, and dried by pulling air through the filter for two to three hours. Finally the material was dried over P_4O_{10} at a temperature of $100^\circ C$ and a pressure of about 250 mm. The yield was 80 percent.

Analysis	C	H
Calculated for tris(1,10-phenanthroline)cobalt(II) perchlorate	54.2 %	3.03%
Found	52.91%	3.09%

Alcoholic Media. 1,10-Phenanthroline is markedly more soluble in ethanol than in water. Consequently, ethanol serves as an ideal solvent for the preparation of tris(1,10-phenanthroline)cobalt(II) perchlorate, since the desired excess of ligand can be completely dissolved in the solvent. Complexation in the tris form is assured and oxidation prevented. The procedure for the preparation of this salt in alcoholic medium is the same as that described for aqueous medium except for the replacement of water by alcohol. The yields are 90 to 100 percent.

Analysis	C	H
Calculated for tris(1,10-phenanthroline)cobalt(II) perchlorate	54.2 %	3.03%
Found	53.72%	3.15%

Tris(1,10-phenanthroline)cobalt(II) Perchlorate Labeled with Cobalt-60

Tris(1,10-phenanthroline)cobalt(II) perchlorate labeled with cobalt-60 for tracer studies was prepared in essentially the same fashion as the inactive material except on a much smaller scale. An appropriate amount of the radioactive stock solution was placed in a 2 ml glass stoppered test tube and heated in a wax bath to remove the hydrochloric acid. After re-

removal of the acid, the tube was allowed to cool and then 500 λ of water was added along with 0.022 grams of 1,10-phenanthroline. The tube was heated slightly to facilitate the dissolution of the ligand. Two hundred lambda of 0.10 M CoCl_2 solution was added to the tube, and a dilute solution of sodium perchlorate added to precipitate the desired perchlorate salt. The material was centrifuged for several minutes and the supernatant liquid removed. Two hundred fifty lambda of water was added to wash the precipitate. The tube was centrifuged and the supernatant liquid removed. The wash procedure was repeated twice.

Tris(1,10-phenanthroline)cobalt(II) Ion Formed *in situ*

The solubility of tris(1,10-phenanthroline)cobalt(II) perchlorate in water is limited (about 10^{-4} M) and frequently higher concentrations of the complex ion were required. Solutions of the complex ion were prepared in situ by the addition of the desired cobaltous salt to an excess of 1,10-phenanthroline. Radioactive as well as inactive solutions were prepared and will be discussed in the appropriate sections.

Tris(1,10-phenanthroline)cobalt(III) Perchlorate

Bromine Oxidation. The method of preparation outlined below is essentially that reported by Pfeiffer and Werdelmann³¹ except that an excess of phenanthroline was employed. Tris(1,10-phenanthroline)cobalt(II) ion is formed in solution and oxidized to the corresponding cobalt(III) complex with bromine. Twenty-five milliliters of 0.10 M CoCl_2 solution was added to about 75 ml of hot water containing 3.0 grams of 1,10-phenanthroline in a 200 ml round bottom flask. The flask was fitted with a condenser and heated to dissolve the excess phenanthroline. Ten milliliters of a saturated solution of bromine water was added and the solution was refluxed

for 30 minutes. Frequently a solid, probably the tribromide, forms but dissolves with continued refluxing. A second 10 ml portion of bromine water was added and the solution refluxed an additional 30 minutes. The hot solution was transferred to a 250 ml beaker and stirred vigorously to remove any excess bromine. A dilute solution of perchloric acid was added to serve as precipitating agent for the cobalt(III) complex, and at the same time to destroy any cobalt(II) complex present. Tris(1,10-phenanthroline)cobalt(III) perchlorate was collected on a medium porosity sintered glass filter, washed with several 15 ml increments of dilute perchloric acid, washed with several 15 ml portions of water, and air dried by pulling air through the filter. Finally, the material was dried over P_4O_{10} at $100^\circ C$ and a pressure of about 250 mm in a drying pistol.

Analysis	C	H
Calculated for tris(1,10-phenanthroline)cobalt(III) perchlorate	48.1 %	2.69%
Found	46.98%	2.73%

Displacement of Ammonia from Hexamminecobalt(III) Salts. Pfeiffer and Werdelmann³¹ heated chloropentamminecobalt(III) chloride and phenanthroline in the absence of solvent, and then dissolved the resulting mass in 30 percent methanol. Concentration of the solution produced tris(1,10-phenanthroline)cobalt(III) chloride. Ellis, Wilkins, and Williams¹³ refluxed chloropentamminecobalt(III) chloride with phenanthroline in 30 percent methanol for up to 40 hours, and were able to produce the desired material. In this work, a method similar to the one reported by Ellis, Wilkins, and Williams was employed for the preparation of tris(1,10-phenanthroline)cobalt(III) perchlorate. One hundred milliliters of water,

1.0 gram of hexamminecobalt(III) nitrate and 3.0 grams of 1,10-phenanthroline were placed in a 200 ml round bottom flask. The flask was fitted with a condenser, heated and allowed to reflux for five days. The precipitation and drying procedures were the same as those described for the bromine oxidation methods. Analysis and spectrum are in agreement with those determined for material obtained by oxidation methods. Yield was 70 percent.

Analysis	C	H
Calculated for tris(1,10-phenanthroline)cobalt(III) perchlorate dihydrate	46.4 %	3.02%
Found	46.65%	3.01%

Chlorine Oxidation. Twenty-five milliliters of 0.10 M CoCl_2 solution was added to 3.0 grams of phenanthroline dissolved in 75 ml of 95 percent ethanol in a 125 ml glass stoppered Erlenmeyer flask. The solution was stirred with a magnetic stirrer, and chlorine was bubbled through for three minutes. The flask was stoppered and allowed to stand for ten minutes. Chlorine was again bubbled through for three minutes, the flask stoppered and allowed to stand for about 30 minutes. A dilute solution of sodium perchlorate in 50 percent ethanol was utilized as precipitating agent. The solid was collected on a medium porosity sintered glass filter. This material was purified by dissolving in hot water and reprecipitating with sodium perchlorate. The purification step is necessary to remove a reddish brown coloration which is believed to be a bis(1,10-phenanthroline)cobalt-(III) species, and is usually employed twice. The ultraviolet spectrum of this material corresponds to those determined for this compound prepared by the other methods.

Hexamminecobalt(III) Nitrate

Hexamminecobalt(III) nitrate was prepared as outlined by a standard synthetic method.³²

Hexamminecobalt(III) Nitrate Labeled with Cobalt-60

Hexamminecobalt(III) nitrate labeled with cobalt-60 was prepared exactly as the inactive material³² except on a much smaller scale. The method is now described. An appropriate amount of cobalt-60 stock solution was placed in a 12 ml centrifuge tube and heated in a wax bath to remove the hydrochloric acid. One ml of water and 0.73 gram of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to the tube followed by one ml of concentrated ammonia solution and 0.80 gram of NH_4NO_3 . A trace of charcoal was added and the solution was oxidized by bubbling oxygen through the solution for ten minutes. An additional ml of water was added and the tube warmed in a water bath. The solution was centrifuged and the liquid removed from the charcoal by means of a transfer pipette. The solution was placed in another 12 ml centrifuge tube and five ml of concentrated nitric acid was added. The tube was cooled and allowed to stand for 30 minutes. The tube was centrifuged and the supernatant liquid removed. The solid was washed with two one-half ml increments of water. This material was reserved for the preparation of cobalt-60 labeled tris(1,10-phenanthroline)cobalt(III) perchlorate.

Tris(1,10-phenanthroline)cobalt(III) Perchlorate Labeled with Cobalt-60

Tris(1,10-phenanthroline)cobalt(III) perchlorate labeled with Co-60 was prepared by the same methods as the inactive material except in much smaller quantities.

Oxidation. A suitable amount of Co-60 stock solution was added to a two ml glass stoppered test tube and heated in a wax bath to remove

hydrochloric acid. After cooling, one ml of water and 0.05 gram of 1,10-phenanthroline were added to the tube and heated on a water bath to facilitate dissolution of the ligand. Two hundred fifty lambda of 0.10 M CoCl_2 solution was slowly added. This solution was oxidized by the addition of several drops of saturated bromine or chlorine water. The tube was allowed to stand for 30 minutes and then heated to remove any excess oxidizing agent. Several drops of a dilute solution of perchloric acid were employed as precipitating agent. The tube was centrifuged and the supernatant liquid removed with a transfer pipette. Five hundred lambda of water was introduced and the tube agitated. The tube was centrifuged and the supernatant liquid was removed. This wash procedure was repeated three times. The solid was used for the preparation of a stock solution.

Displacement of Ammonia from Hexamminecobalt(III) Nitrate Labeled with Cobalt-60. Approximately 0.1 gram of labeled hexamminecobalt(III) nitrate was placed in a 25 ml round bottom flask and ten milliliters of water was added. To this solution was added one gram of 1,10-phenanthroline. The flask was fitted with a condenser, heated and allowed to reflux for 24 hours. The solution was transferred to a 25 ml centrifuge cone and dilute perchloric acid was added dropwise to precipitate the desired material. The material was allowed to settle and the supernatant liquid removed. The solid was washed with five one ml increments of water. This material was used for the preparation of a stock solution.

Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(II) Perchlorate

To 3.65 grams of 3,4,7,8-tetramethyl-1,10-phenanthroline dissolved in 200 ml of absolute ethanol was slowly added a 50 percent alcoholic solution (approximately 25 ml) containing 0.74 gram of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. A dilute

50 percent ethanolic solution of sodium perchlorate was added to precipitate tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(II) perchlorate. The compound was collected on a medium porosity sintered glass filter. The precipitate is gelatinous and filtration is extremely difficult. The material on the filter was washed with ten 20 ml portions of hot ethanol to remove any excess ligand present. The compound was air dried and then dried over P_4O_{10} in a drying pistol at $100^\circ C$ and a pressure of approximately 200 mm. The yields are 95 percent.

Analysis	C	H
Calculated for tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(II) perchlorate dihydrate	57.49%	5.22%
Found	53.43%	5.18%

The analytical data are not consistent with any particular formula, even taking into account the possibility of hydration of variable degree. The sample probably contained some of the cobalt(III) complex.

Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III) Perchlorate

Chlorine Oxidation. To 3.65 grams of 3,4,7,8-tetramethyl-1,10-phenanthroline in 80 ml of absolute ethanol was added 0.74 gram of $CoCl_2 \cdot 6H_2O$ in 20 ml of water. The resulting cobaltous complex was stirred with a magnetic stirrer and oxidized by bubbling chlorine through the solution for three minutes. The solution was stoppered and stirred for ten minutes. Chlorine was bubbled through the solution an additional three minutes. The solution was allowed to stand 30 minutes and then a dilute 50 percent ethanolic solution of sodium perchlorate was added to precipitate tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III) perchlorate. The

material was collected on a medium porosity sintered glass filter and washed with ten 20 ml portions of hot ethanol. The solid was air dried by pulling air through the filter and then dried over P_4O_{10} in a drying pistol at $100^\circ C$ and a pressure of about 250 mm. The yield was 95 percent.

Analysis	C	H	N
Calculated for tris(3,4,7,8-tetramethyl-1,10- phenanthroline)cobalt(III) perchlorate dihydrate	52.3 %	4.72%	7.61%
Found	51.75%	4.66%	7.14%

Displacement of Ammonia from Hexamminecobalt(III) Nitrate. Attempts to prepare this compound by the displacement of ammonia from hexamminecobalt(III) nitrate similar to the preparation of the unsubstituted phenanthroline complex failed. However, this procedure was not pursued extensively.

Tris(5-nitro-1,10-phenanthroline)cobalt(II) Perchlorate

To 4.75 grams of 5-nitro-1,10-phenanthroline in 200 ml of hot ethanol was slowly added 1.00 gram of $CoCl_2 \cdot 6H_2O$ contained in about 40 ml of 50 percent ethanol. The solution was filtered and a dilute solution of 50 percent ethanolic sodium perchlorate was added to precipitate tris(5-nitro-1,10-phenanthroline)cobalt(II) perchlorate. The compound was collected on a sintered glass filter and washed with ten 20 ml portions of hot ethanol. The material was then air dried and finally dried in a drying pistol over P_4O_{10} at $100^\circ C$ and a pressure of approximately 250 mm. The yields are 95 percent.

Analysis	C	H	N
Calculated for tris(5-nitro-1,10-phenanthroline)- cobalt(II) perchlorate	46.32%	2.27%	13.51%
Found	46.19%	2.56%	13.75%

Tris(5-nitro-1,10-phenanthroline)cobalt(III) Perchlorate

Chlorine Oxidation. A 50 percent ethanolic solution containing 0.64 gram of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was slowly added to 3.00 grams of 5-nitro-1,10-phenanthroline in 150 ml of ethanol. Chlorine was bubbled through the stirred solution for three minutes and the solution was allowed to stand for ten minutes. The oxidation procedure was repeated and a dilute 50 percent ethanolic solution of sodium perchlorate was employed as precipitating agent. The precipitate was collected on a sintered glass filter and washed with ten 20 ml portions of hot ethanol. The solid was air dried and then dried over P_4O_{10} in a drying pistol at 100°C and a pressure of approximately 250 mm. The yield was 70 percent.

Analysis	C	H	N
Calculated for			
tris(5-nitro-1,10-phenanthroline)-			
cobalt(III) perchlorate trihydrate	39.78%	2.50%	11.60%
Found	40.17%	2.63%	11.29%

Displacement of Ammonia from Hexamminecobalt(III) Nitrate. Attempts to prepare this compound by the displacement method failed.

Spectra

Spectra of 1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, 5-nitro-1,10-phenanthroline, and the corresponding tris complexes of cobalt(II) and cobalt(III) were determined in the range 200-1200 millimicrons employing a Cary Model 14 recording spectrophotometer.

1,10-Phenanthroline

Ultraviolet Region. 1,10-Phenanthroline was recrystallized from water and air dried. The compound was then dried in a desiccator over

calcium chloride and potassium hydroxide. A solution prepared by dissolving 0.00276 gram of this material in 500 ml of water was used for the measurement of the spectrum.

Visible and Near Infrared Region. The spectrum of a 1.17×10^{-2} M solution of 1,10-phenanthroline in water was determined in the visible and near infrared regions employing ten centimeter cells.

Tris(1,10-phenanthroline)cobalt(II)

Ultraviolet Region. A solution was prepared by dissolving 0.1518 gram of tris(1,10-phenanthroline)cobalt(II) perchlorate monohydrate in two liters of water. Fifty milliliters of this solution was diluted to 500 ml and the spectrum of the diluted solution determined in a one centimeter cell. Cells of longer path lengths and more concentrated solutions were employed to determine shoulders in this region of the spectrum.

Visible and Near Infrared Region. For determination of the visible and near infrared spectra a solution of tris(1,10-phenanthroline)cobalt-(II) ion was prepared in situ by slowly adding 0.899 gram of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in approximately 30 ml of water to 3.00 grams of 1,10-phenanthroline in 50 ml of water. The final volume was adjusted to 100 ml. Spectra were measured using one and five centimeter cells. Spectra in this region were also determined in 50 percent ethanol. Ten milliliters of 0.074 M aqueous CoCl_2 solution was added to 0.70 gram of 1,10-phenanthroline dissolved in 25 ml of absolute ethanol and the final volume adjusted to 50 ml. Spectra were determined employing 50 percent ethanol in the reference cell.

Tris(1,10-phenanthroline)cobalt(III)

Ultraviolet Region. A solution was prepared by dissolving 0.2216

gram of tris(1,10-phenanthroline)cobalt(III) perchlorate in two liters of water. Fifty milliliters of this solution was diluted to 500 ml and the spectrum of the diluted solution determined in a one centimeter cell. More concentrated solutions and longer path lengths were employed to determine shoulders in the ultraviolet region.

Visible and Near Infrared Region. In this region a more concentrated solution was needed than could be attained from the perchlorate. To 2.24 grams of the perchlorate in 25 ml of water was added three grams of Dowex 1-X8 anion exchange resin in the chloride form to convert the perchlorate to the more soluble chloride. When conversion was complete, as indicated by the disappearance of the solid perchlorate and the development of color in the solution, the resin was removed by filtration and the final solution adjusted to a volume of 50 ml. Spectra were determined in the region 400-1150 millimicrons on this solution and others prepared by quantitative dilutions.

3,4,7,8-Tetramethyl-1,10-phenanthroline

Ultraviolet Region. 3,4,7,8-Tetramethyl-1,10-phenanthroline was recrystallized from an ethanol-water mixture. The compound was collected on a sintered glass filter funnel and dried over P_4O_{10} in a drying pistol at 100° C and a pressure of approximately 250 mm.

Analysis	C	H
Calculated for		
3,4,7,8-tetramethyl-1,10-phenanthroline	81.35%	6.78%
Found	81.29%	7.01%

A solution was prepared by dissolving 0.000810 gram in 100 ml of water. The ultraviolet spectrum was determined in a one centimeter cell.

Visible and Near Infrared Region. The visible and near infrared spectra were determined in 50 percent ethanol in order to attain a greater solubility of 3,4,7,8-tetramethyl-1,10-phenanthroline. Spectra were determined on a solution which contained 0.2028 gram in 50 ml employing ten centimeter cells.

Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(II)

Ultraviolet Region. To 0.01060 gram of tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(II) perchlorate in 50 ml of water was added 0.5 gram of Dowex 1-X8 anion exchange resin in the chloride form. The perchlorate was converted to the more soluble chloride. The resin was removed and the solution diluted to one liter in a volumetric flask. The spectrum of the diluted solution was determined in the ultraviolet region.

Visible and Near Infrared Region. A solution of tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(II) chloride was prepared in situ by dissolving 0.6 gram of 3,4,7,8-tetramethyl-1,10-phenanthroline in 25 ml of absolute ethanol followed by the addition of 10 ml of 0.074 M CoCl_2 solution and 15 ml of water. Spectra were determined in the range 500-1150 millimicrons employing ten centimeter cells.

Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III)

Ultraviolet Region. A solution was prepared by dissolving 0.01106 gram of tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III) perchlorate in one liter of water. The spectrum was determined employing a one centimeter cell.

Visible and Near Infrared Region. To 1.87 grams of tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III) perchlorate in 50 ml of water was added two grams of Dowex 1-X8 anion exchange resin in the chloride

form. The perchlorate salt was converted to the more soluble chloride and the resin removed by filtration. The resulting solution was diluted to 100 ml and the spectra in the visible and near infrared regions determined in cells of various path lengths.

5-Nitro-1,10-phenanthroline

Ultraviolet Region. A solution of 5-nitro-1,10-phenanthroline was prepared by dissolving 0.1074 gram of this compound in 25 ml of absolute ethanol followed by dilution to 50 ml. Ten milliliters of this solution was diluted to one liter with water, and the spectrum of the diluted solution determined.

Visible and Near Infrared Region. A solution containing 0.1949 gram of 5-nitro-1,10-phenanthroline in 100 ml of 50 percent ethanol was prepared and the spectrum measured.

Tris(5-nitro-1,10-phenanthroline)cobalt(II)

Ultraviolet Region. A solution was prepared by adding 0.5 gram of Dowex 1-X8 anion exchange resin in the chloride form to 0.0101 gram of tris(5-nitro-1,10-phenanthroline)cobalt(II) perchlorate in 100 ml of water and stirring with a magnetic stirrer to facilitate dissolution. The resin was removed by filtration and the solution diluted to one liter. The spectrum of the diluted solution was measured in a one centimeter cell.

Visible and Near Infrared Region. A solution of tris(5-nitro-1,10-phenanthroline)cobalt(II) ion was prepared in situ by partly dissolving 0.72 gram of 5-nitro-1,10-phenanthroline in 25 ml of absolute ethanol and adding 10 ml of 0.074 M CoCl_2 solution followed by 15 ml of water. The spectrum of this solution was measured in a ten centimeter cell with 50 percent ethanol in the reference cell.

Tris(5-nitro-1,10-phenanthroline)cobalt(III)

Ultraviolet Region. A solution of tris(5-nitro-1,10-phenanthroline)-cobalt(III) was prepared by adding five grams of Dowex 1-X8 anion exchange resin in the chloride form to 2.325 grams of tris(5-nitro-1,10-phenanthroline)cobalt(III) perchlorate in 50 ml of water and stirring with a magnetic stirrer. The resin was removed by filtration and the solution diluted to a volume of 100 ml. This solution was diluted by a factor of 2500 and the spectrum of the diluted solution determined.

Visible and Near Infrared Region. Eight milliliters of the stock solution described in the preceding section was diluted to 50 ml and the spectrum determined in a one centimeter cell.

Resolution of Cobalt(III) Phenanthroline Complexes

Until recently no tervalent phenanthroline complex had been resolved into its enantiomorphic forms. Hunt³³ has successfully resolved the tris(1,10-phenanthroline)chromium(III) ion by employing mixed solvents to decrease the solubility of tris(1,10-phenanthroline)chromium(III) antimonyl tartrate. This method was employed for cobalt(III) complexes and is described now.

Tris(1,10-phenanthroline)cobalt(III) Ion

Sixty milliliters of water at a temperature of approximately 60° C was added to 3.00 grams of tris(1,10-phenanthroline)cobalt(III) perchlorate prepared by the chlorine oxidation method. The temperature was allowed to decrease to 50° C and 5.0 grams of 200-400 mesh Dowex 1-X8 anion exchange resin in the chloride form was added with stirring. The resin has a great affinity for perchlorate ions and conveniently converts the difficultly

soluble perchlorate salt to the more soluble chloride. The mixture was stirred with a magnetic stirrer until all of the cobalt salt was dissolved, and then the resin was removed by filtering the solution through a medium porosity sintered glass filter. The resin was washed with several 5 ml increments of water. The volume of the resulting filtrate and washings was approximately 100 ml.

Four grams of silver antimonyl tartrate was introduced to the solution to serve as resolving agent. The resulting silver chloride was removed by filtration and washed with several 10 ml portions of water; the volume of the resultant filtrate was approximately 200 ml. The solution was heated to 55° C, and ethanol was added to decrease the solubility of tris(1,10-phenanthroline)cobalt(III) antimonyl tartrate. The ethanol was added slowly with stirring until cloudiness occurred; the total volume of solution was about 520 ml and the temperature 40° C. The material was stirred frequently and allowed to cool to room temperature, 20° C. The precipitate was recovered by filtration, washed with ethanol several times, and dried by pulling air through the filter. Fraction A weighed 2.44 grams. The filtrate was saved for further treatment in an attempt to recover the more soluble isomer. The first fraction was dissolved in 60 ml of water and filtered to remove insoluble material. Fractional precipitation was repeated with fraction B weighing 1.33 grams. A 0.02306 gram sample of this fraction in 10 ml of water produced a rotation of $-0.85 \pm 0.02^\circ$ when measured in a one decimeter cell at the sodium line employing a Bellingham and Stanley polarimeter. An additional fractionation produced 1.11 grams of material, fraction C. A rotation of $-0.78 \pm 0.02^\circ$ was recorded for a 0.0237 gram sample in 10 ml of water. Constancy of rotation was considered

to indicate complete resolution, and no additional fractionations were conducted.

Fraction C was dissolved in 100 ml of water and an excess of sodium perchlorate solution was added. Tris(1,10-phenanthroline)cobalt(III) perchlorate precipitated while the resolving agent remained in solution. The compound was collected on a sintered glass filter, washed with 10 ml portions of water several times, and then washed with 20 ml of absolute ethanol. The sample was dried by pulling air through the filter. The resulting tris(1,10-phenanthroline)cobalt(III) perchlorate weighed 0.50 gram.

A large excess of sodium perchlorate was added to the filtrate from the first fractionation to recover as much of the tris(1,10-phenanthroline)-cobalt(III) ion remaining in solution as possible and to attempt to isolate the more soluble isomer. The precipitate was collected on a sintered glass filter and dried. The resulting material weighed 0.60 gram. This solid was dissolved in 50 ml of water and cooled in an ice bath. A solution of sodium perchlorate was added dropwise until cloudiness resulted. Then the calculated amount (0.10 gram) of sodium perchlorate was added to precipitate one-half the tris(1,10-phenanthroline)cobalt(III) ion in solution. The solid (0.28 gram) was removed by filtration and an excess of precipitating agent was added. The final precipitate was collected, washed, and dried as previously, with 0.092 gram of solid resulting. The rotation of a solution containing 0.092 gram in 100 ml of water measured in a two decimeter cell at the sodium line was $+0.32^\circ$ and indicates that pure d-tris(1,10-phenanthroline)cobalt(III) was not obtained.

Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III) Ion

The resolution procedure described for tris(1,10-phenanthroline)-

cobalt(III) ion was employed for the corresponding 3,4,7,8-tetramethyl-1,10-phenanthroline complex. Partial resolution was accomplished readily; however, efforts were not vigorously pursued to accomplish complete resolution.

For the resolution of this compound the volume of water employed should be minimized. If the volume is large, frequently the desired tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III) antimonyl tartrate will not precipitate upon the addition of ethanol. Another obstacle is that, once the antimonyl tartrate salt is obtained, difficulty is encountered preparing solutions for refractionation. This difficulty in dissolution may be a kinetic effect. Also, a sample of the antimonyl tartrate salt which had been partially resolved racemized in less than a month.

Tris(5-nitro-1,10-phenanthroline)cobalt(III) Ion

Attempts to resolve this material have proved unsuccessful.

Asymmetric Synthesis of Tris(1,10-phenanthroline)cobalt(III)

Recently H. R. Hunt³³ demonstrated that antimonyl tartrate preferentially precipitated the labile tris(1,10-phenanthroline)chromium(II) ion in one stereoisomer which could be oxidized to the corresponding chromium(III) compound. This procedure has been utilized for tris(1,10-phenanthroline)cobalt(II) ion and is now described.

To 2.40 grams of 1,10-phenanthroline monohydrate dissolved in 250 ml of hot water was added 0.48 gram of cobaltous chloride hexahydrate in 30 ml of water. Additional water was added until the volume was about 450 ml; the solution was heated to 55° C. One gram of potassium antimonyl tartrate was added in a small quantity of water. A solution was obtained; however, a precipitate occurred in about two minutes. This precipitate was dissolved

by addition of water to give a total volume of 800 ml and heating to 80° C. The solution was allowed to cool to room temperature and the precipitate collected on a sintered glass filter. The resultant solid was transferred to a 200 ml Erlenmeyer flask containing 100 ml of ethanol and oxidized with chlorine. The solid was collected on a sintered glass filter and air dried; two grams of material resulted. The oxidized material was dissolved in 100 ml of water, filtered, and then converted to tris(1,10-phenanthroline)-cobalt(III) perchlorate by the addition of a solution of sodium perchlorate. The solid weighed 0.82 gram and represented a yield of 45 percent.

The rotation of a solution prepared by dissolving 0.1022 gram in 100 ml of water was observed to be +0.75° when measured in a two decimeter tube at the sodium line.

Optical Rotatory Dispersion

Optical rotatory dispersion curves were determined for the resolved or partially resolved complexes employing a Perkin-Elmer ORD attachment in conjunction with a Cary Model 14 recording spectrophotometer.

Tris(1,10-phenanthroline)cobalt(III)

A solution of 1-tris(1,10-phenanthroline)cobalt(III) perchlorate was prepared by dissolving 0.2007 gram of the salt in water to make a total volume of 100 ml. Rotation at the sodium line was found to be -3.07° in a two decimeter cell employing a polarimeter. This rotation corresponds to a specific rotation of -765.

Optical rotatory dispersion was measured over the wavelength range 400-650 millimicrons with a setting of 80° for the prisms of the ORD attachment. The dispersion curve was normalized to correspond to the value

of the specific rotation obtained at the sodium line employing a Bellingham and Stanley polarimeter.

Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III)

Optical rotatory dispersion was measured for the partially resolved d-stereoisomer and found to be almost exactly identical with d-tris(1,10-phenanthroline)cobalt(III) ion.

Magnetic Susceptibility

Magnetic susceptibilities of tris(1,10-phenanthroline)cobalt(II) perchlorate and the corresponding complexes containing 3,4,7,8-tetramethyl-1,10-phenanthroline and 5-nitro-1,10-phenanthroline were determined by the Gouy method.³⁴ A Newport four inch electromagnet was employed in conjunction with a Newport power supply. A current of 6.0 amperes was used in the magnet coils, providing a field strength of approximately 10,000 gauss. Weighings were accomplished with a Mettler balance capable of weighing to one one-hundredth of a milligram. The magnetic field and sample tube parameters were calibrated by utilizing $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a standard. All measurements were conducted at room temperature. Data are recorded in Table 2.

Electron Transfer Reactions

Exchange reactions such as the systems studied in this work undergo no net chemical change and, consequently, the kinetics cannot be studied by conventional methods which detect a change in the amount of a product or reactant. Two methods which are frequently employed in investigations of reactions of this type are isotopic exchange and the measurement of the change of optical rotation. These methods are employed in this study.

Table 2. Magnetic Susceptibility Data

Specimen	Magnet	Weight in Grams
Tube	off	12.03244
Tube	on	12.02549
Tube + standard	off	13.94498
Tube + standard	on	14.05262
Tube + tris(1,10-phenanthroline)cobalt-(II) perchlorate	off	12.79043
	on	12.81784
Tube + tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(II) perchlorate	off	12.52045
	on	12.52824
Tube + tris(5-nitro-1,10-phenanthroline)cobalt(II) perchlorate	off	12.46780
	on	12.47645

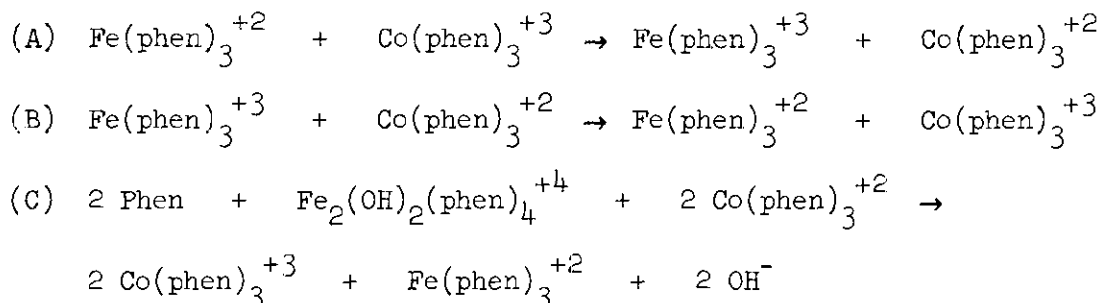
Isotopic Exchange

In an isotopic exchange reaction, the isotopic atoms must possess a measurable difference in some property. If a convenient radioactive isotope is available, exchange is measured by the change in the amount of radioactivity in one of the exchanging species. In such an experiment, the exchanging species must be capable of at least partial separation. Samples are collected at varying times, the exchanging species separated, and the amount of exchange determined.

Development of Procedure. The first exchange system chosen for study employed unsubstituted phenanthroline as ligand. Previous work¹⁴ on this system indicated that the rate was quite fast and that half-times of the order of minutes would be obtained only by operating at temperatures below room temperature and by keeping the concentrations of the complexes in the range 10^{-3} to 10^{-6} M. Numerous preliminary exchange runs using the radiochemical tracer technique gave erratic results and could not be reproduced. A long sequence of investigations revealed factors which contributed to the erratic behavior of the system and led to the procedure finally adopted for the measurement of the rate.

A metal ion capable of existing in more than one oxidation state can serve to catalyze the exchange reaction if it can be both oxidized and reduced by the components of the system. The erratic behavior seemed to be more pronounced when an excess of phenanthroline was present in the system. This can be interpreted to indicate that a metal ion impurity is functioning as a catalyst more proficiently when present as a phenanthroline complex. Since iron is a frequent laboratory contaminant, as well as an impurity in cobalt salts and satisfies the multi-oxidation state requirement, the fol-

lowing reactions of phenanthroline complexes of iron and cobalt were investigated:



Reaction (A) does not take place but reactions (B) and (C) do occur. Reactions (B) and (C) have been studied by other investigators;³⁵ their results are in agreement with the above. If iron in the ferric state is present as an impurity, it will exist as the binuclear species, $\text{Fe}_2(\text{OH})_2(\text{phen})_4^{+4}$, in the presence of phenanthroline; this species is always the product formed by direct combination of phenanthroline and ferric ions, and Fe(phen)_3^{+3} is never formed in this fashion. The binuclear ferric species can react with the cobalt(II) species; however, since reaction (A) does not occur, the ferrous species formed by reaction (C), or any ferrous complex initially present, does not possess a path by which it can be oxidized to a ferric species. Consequently, iron cannot serve to catalyze the exchange reaction. Furthermore, it is difficult to select other metal ions which are common impurities in cobalt salts and exist in more than one oxidation state. Of course, ferric impurities will react according to reaction (C) and consume some of the cobalt(II) species present. Metal ion impurities are not thought to be responsible for the erratic behavior.

The tris(1,10-phenanthroline)cobalt(III) ion is inert to substitution¹³ and presumably thermodynamically stable. Consequently, little thought was devoted to the possibility that a solution of this material

would be chemically altered on standing. However, spectral evidence indicates that a solution of tris(1,10-phenanthroline)cobalt(III) ion is, in fact, partially reduced if allowed to age under ordinary laboratory conditions for several months. This reduction can be accelerated if illuminated with an ordinary 200 watt incandescent lamp for a day at a distance of one foot. The reaction may be photochemical in nature or reduction may be caused by organic matter in solution.

In exchange runs for the determination of the rate dependence on Co(III) the concentration of Co(III) is as much as one hundred times the concentration of the Co(II) complex. As a consequence, a small amount of reduction of the Co(III) complex to the corresponding Co(II) complex will generate as much of this material as was initially present in the reaction mixture. This will drastically affect the results. To alleviate the possibility of partial reduction of the Co(III) species which would lead to erroneous, if not erratic results, no Co(III) solution was employed if aged over two days. All Co(III) solutions were stored in the dark and reaction vessels were painted black to minimize exposure of the solutions to light. Also, water distilled from acid dichromate and basic permanganate was employed.

The presence of excess phenanthroline in the system is necessary to insure complete complexation of the Co(II) in the tris form. In early experiments the excess ligand was incorporated in the stock solution of inert electrolyte and added to the Co(II) solution prior to the exchange reaction. This method of addition of phenanthroline is very convenient and allows the determination of its concentration from the ultraviolet spectrum of the stock solution which contains neither of the cobalt complexes.

Phenanthroline in such a solution was not expected to undergo reaction at normal laboratory conditions; however, a saturated solution of phenanthroline was accidentally exposed to bright sunlight for several hours and a yellow coloration noted. A brownish deposit resulted when the water was allowed to evaporate at room temperature. Several drops of a solution of this material were added to an exchange run and the rate was markedly increased. The effect on the rate is displayed in Figure 1; the two exchange reactions are the same in every respect except for the added reaction product of phenanthroline. The concentrations of the species are: $\text{tris}(1,10\text{-phenanthroline})\text{cobalt(II)} = 2.2 \times 10^{-5} \text{ M}$, $\text{tris}(1,10\text{-phenanthroline})\text{cobalt(III)} = 8.0 \times 10^{-5} \text{ M}$, and 0.01 M sodium perchlorate serving as inert electrolyte. To eliminate the possibility that increased rates of exchange might be promoted by aged solutions of phenanthroline, in all subsequent reactions the solid ligand was added to the $\text{tris}(1,10\text{-phenanthroline})\text{cobalt(II)}$ solution only about 30 minutes prior to the exchange reaction.

A sequence of reactions was conducted in which the only variable was the concentration of excess phenanthroline. The data are presented in Figure 2 as a plot of the slope (from McKay equation) versus the concentration of excess ligand. See pages 65 - 66 for a discussion of McKay equation. The concentration of $\text{tris}(1,10\text{-phenanthroline})\text{cobalt(II)}$ is 1.78×10^{-5} , the concentration of $\text{tris}(1,10\text{-phenanthroline})\text{cobalt(III)}$ varies but is about 2×10^{-4} for all reactions, and sodium perchlorate was employed to maintain a constant ionic atmosphere of 0.01 M. Even though these reactions were conducted when the procedure for conducting an exchange had not been finalized, the results can be interpreted in a

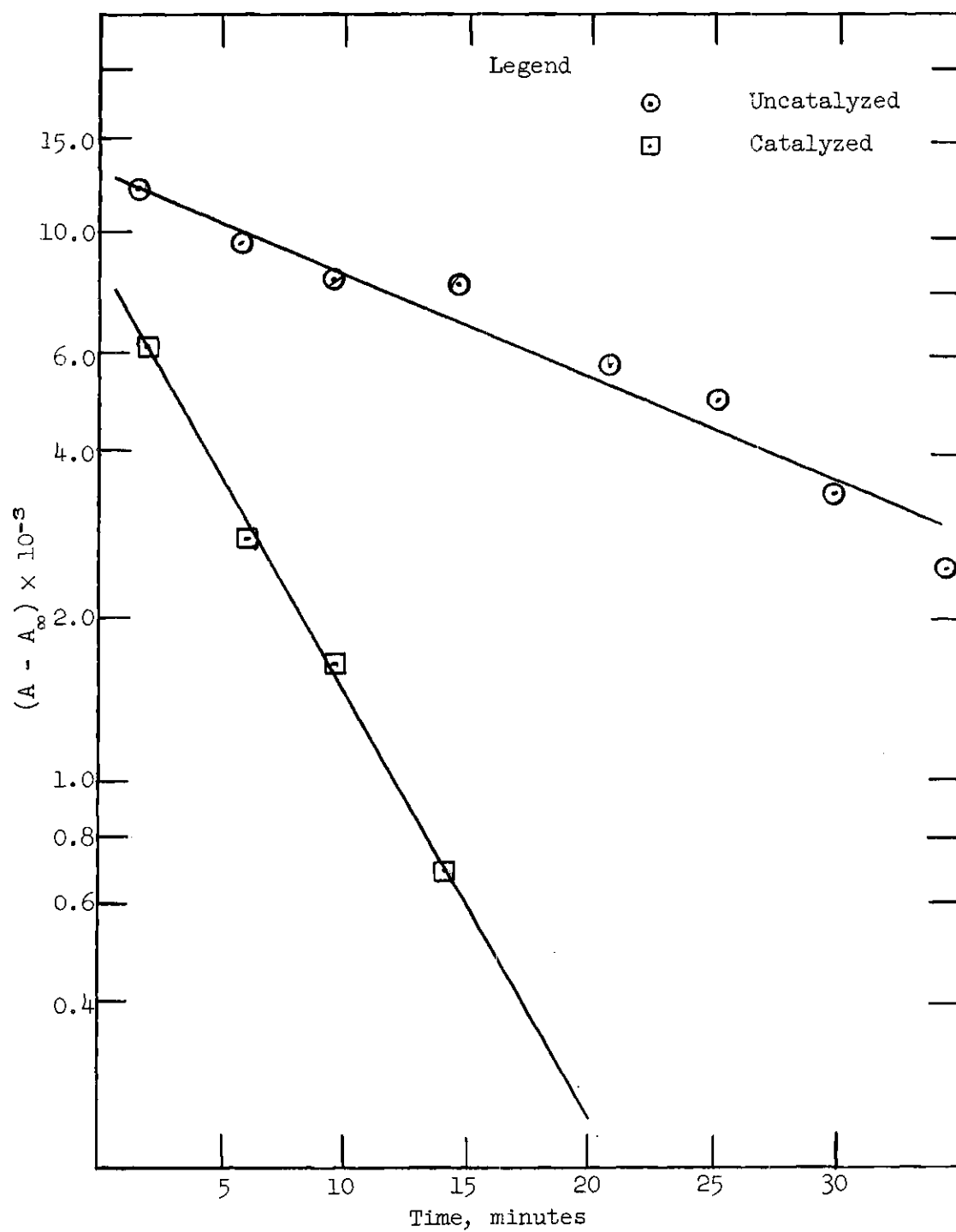


Figure 1. Catalytic Exchange

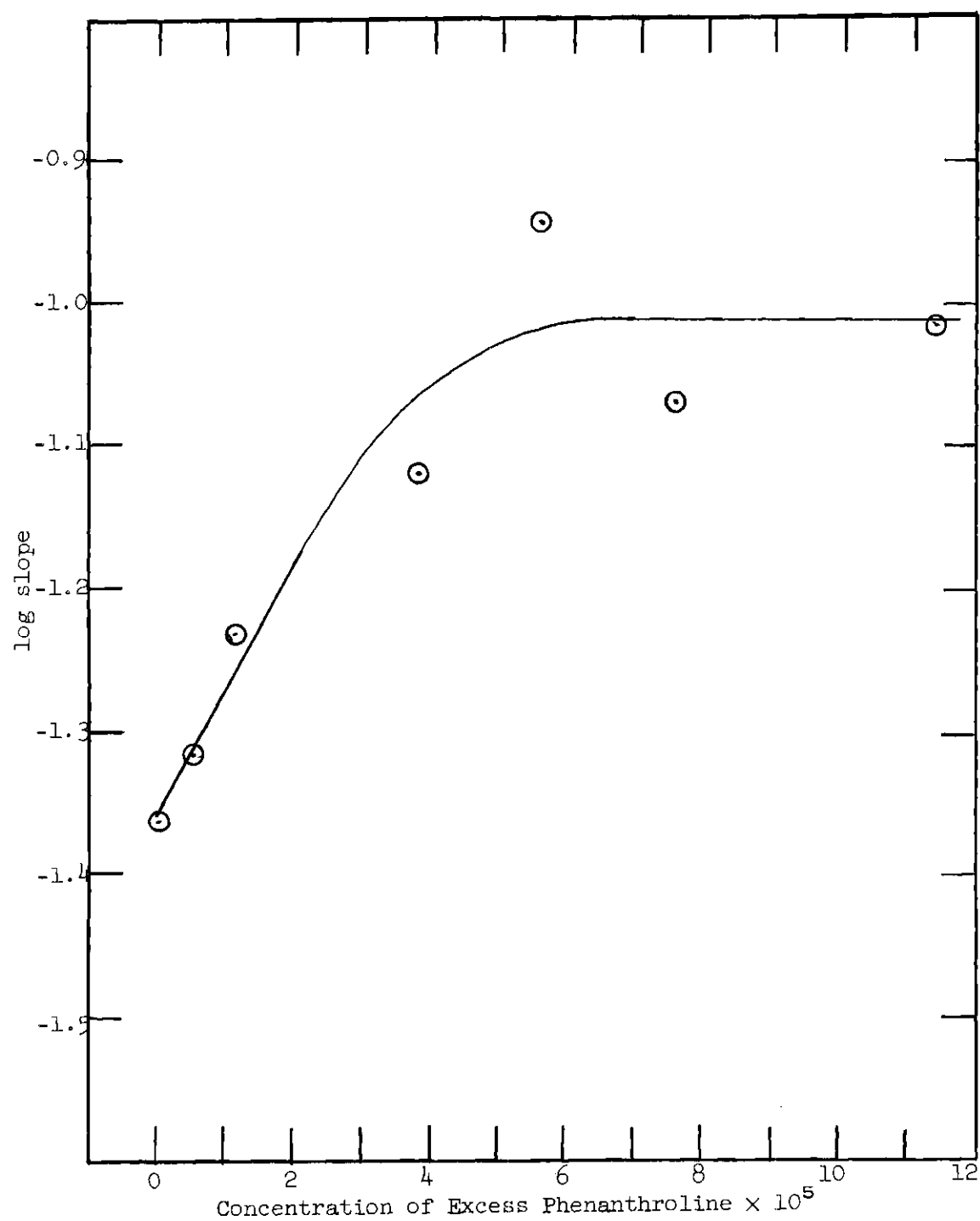


Figure 2. Dependence of Rate on Concentration of Excess Phenanthroline

qualitative sense. The data seem to indicate that the tris cobaltous species reacts at a faster rate than lower complexes. The plateau indicates that the excess phenanthroline has no further effect once the tris species is completely formed.

Visual observations indicate that cobaltous solutions containing phenanthroline are highly susceptible to air oxidation when the mole ratio of cobalt to phenanthroline is one to two. This is in contrast to the difficulty encountered when attempting to air oxidize cobaltous ions in the presence of excess phenanthroline. Tris(1,10-phenanthroline)cobalt(II) is labile and, consequently, dissociates in solution. If an excess of phenanthroline is not present, air oxidation can occur through the bis species. To eliminate the possibility of air oxidation, solutions of tris(1,10-phenanthroline)cobalt(II) should always contain an excess of ligand. Spectrophotometric studies indicate that four or five moles of ligand per mole of metal ion are sufficient. One must decide whether the excess phenanthroline should be added as the solid at the time of reaction to prevent aging of the phenanthroline solution or should be present in the cobaltous complex solution to prevent air oxidation. The latter is believed to be more desirable.

The procedure for conducting an exchange reaction was modified to include the recommendations of the previously described preliminary experiments. Several reactions were conducted and the rates of duplicate runs were observed to decrease. This is in contrast to earlier runs in which rates became progressively more rapid. The only solution aging rapidly was the freshly prepared tris(1,10-phenanthroline)cobalt(III) solution. A careful study was conducted and the data are collected in the following

table. The reactions were conducted at 10° C and a concentration of 1.0×10^{-4} M sodium sulfate was employed as inert electrolyte. The concentrations of the cobalt(II) and cobalt(III) complexes were 1.92×10^{-5} M and 3.61×10^{-4} M, respectively.

Age of Co(III) Solution in minutes	Slope min^{-1}	$t_{1/2}$ minutes	Activity at infinite time
90	1.39×10^{-1}	4.92	2100
465	1.10×10^{-1}	6.33	2114
1455	0.95×10^{-1}	7.33	2096

The cobalt(III) utilized in this series was prepared by bromine oxidation of the corresponding cobalt(II) complex in an excess of phenanthroline.

Another series of reactions was conducted, but the cobalt(III) employed was prepared by displacing the ammonia from hexamminecobalt(III) nitrate by phenanthroline. Detailed preparative procedures for the cobalt(III) complexes are contained in another section. The data are presented in the following table. The reactions were conducted at 15° C in a solution of 0.01 M KClO_4 to maintain a constant ionic atmosphere. The cobalt(II) concentration was 1.92×10^{-5} M and that of cobalt(III) 3.43×10^{-4} M.

Age of Solution in minutes	Slope min^{-1}	$t_{1/2}$ minutes	Activity at infinite time
65	9.11×10^{-2}	7.50	1805
505	9.15×10^{-2}	7.66	1808
1365	9.41×10^{-2}	7.42	1849
3000	9.16×10^{-2}	7.66	1820

Tris(1,10-phenanthroline)cobalt(III) perchlorate was prepared by chlorine oxidation of the corresponding cobalt(II) complex in an excess of

phenanthroline. Several kinetic runs were conducted and the results are comparable to reactions which employed tris(1,10-phenanthroline)cobalt(III) perchlorate prepared by the displacement of ammonia from hexaminecobalt(III) nitrate. Also, no change in rate was noted with the age of the cobalt(III) solution.

Tris(1,10-phenanthroline)cobalt(III) ion is more easily prepared by chlorine oxidation than by the displacement of ammonia from hexaminecobalt(III) nitrate, and was employed in the isotopic exchange reactions since the results were comparable to those obtained when the cobalt(III) complex prepared by the displacement procedure was utilized.

Measurement of Rate. The reactions were conducted in the following manner: the reactants and inert electrolyte were thermostated in a constant temperature bath which controlled the temperature to within 0.05° C. Twenty-five milliliter glass stoppered Erlenmeyer flasks painted black to eliminate possible photochemical effects served as storage containers as well as reaction vessels. Volumes of solutions utilized were 2 ml for the inert electrolyte, and 4 and 5 ml for the cobalt species, depending on which was radioactive. The order of mixing of the cobalt species is immaterial, but the radioactive species was added first for convenience. The reaction was initiated by adding the inactive cobalt species to the reaction vessel containing the inert electrolyte and the radioactive cobalt species. When one-half of the final reactant had been added, a stop watch was started to measure the elapsed time.

Samples were taken from the reaction mixture at varying times and prepared for counting in the following manner. A sample was withdrawn from the reaction vessel in a 500λ micropipette affixed to a one cc syringe

through a rubber stopper. The contents (since the pipette is calibrated to contain a certain volume and not to deliver this volume, the volume delivered is slightly less than 500 λ , but is constant in all experiments) of the micropipette was discharged into a 2 ml glass stoppered test tube containing 250 λ of 2.0 M hydrochloric acid which served to quench the reaction. The time of quenching was noted. The acid destroys the tris-(1,10-phenanthroline)cobalt(II) complex and converts it to chloro complexes such as CoCl_3^- and CoCl_4^{2-} . These species do not exchange with the tris-(1,10-phenanthroline)cobalt(III) ion, which is unchanged in the acid medium.

A 250 λ aliquot of 4.0 M sodium thiocyanate solution was added to the acidic solution and the cobaltous species were converted to the thiocyanate complex, $\text{Co}(\text{SCN})_4^{2-}$. One milliliter of methyl isobutyl ketone was added to the tube and the mixture vigorously hand-shaken for 30 seconds. The test tube was then placed in a centrifuge for 30 seconds to facilitate separation of the aqueous and organic phases. At least 90 percent of the cobaltous complex was extracted into the organic phase while 95 percent of the tris(1,10-phenanthroline)cobalt(III) ion remained in the aqueous portion. A 500 λ portion of the organic phase was withdrawn and placed in a small test tube. The micropipette was rinsed with 500 λ of methyl isobutyl ketone, and the washings were added to the solution in the test tube. The solution was then set aside for counting. Additional samples were withdrawn and treated similarly. The number of samples per run varied depending upon the rate of the reaction, but normally six to twelve were collected. At least ten half-times were allowed to elapse before infinite time samples were taken.

A Nuclear Chicago Model 184 scaling unit in conjunction with a well-

type sodium iodide scintillation detector was employed for determining the amount of cobalt-60 in the samples. Each sample was counted at least twice for a duration of two minutes.

The method of calculating rate constants from the experimental data will be described in the next chapter.

Racemization

In electron transfer systems the rate of racemization of an optically active reactant can be related to the rate of electron transfer. Reactions were conducted in the following manner. The reactants and inert electrolyte were thermostatted in a constant temperature bath. To 15 ml of the cobalt(II) complex was added 10 ml of 0.40 M KNO_3 solution which served to maintain a constant ionic atmosphere. Then 15 ml of the optically active cobalt(III) complex was added. A stop watch was initiated to measure elapsed time when one-half of this solution had been delivered. The solution was mixed well and the change in rotation versus time was measured.

Measurements in the system consisting of tris(1,10-phenanthroline)-cobalt(II) ion, tris(1,10-phenanthroline)cobalt(III) ion were made employing a Perkin-Elmer ORD attachment in conjunction with a Cary Model 14 recording spectrophotometer equipped with thermostatted cell compartments. All measurements were made in a matched pair of five centimeter silica cells at 510 millimicrons.

Rotations in the system employing 3,4,7,8-tetramethyl-1,10-phenanthroline were made with a Bendix recording polarimeter. A jacketed cell of approximately five centimeters length was employed for all measurements.

CHAPTER III

RESULTS

SpectraUltraviolet Spectra of 1,10-Phenanthroline and the Corresponding Tris-Cobalt(II) and Cobalt(III) Complexes

1,10-Phenanthroline. The spectrum of 1,10-phenanthroline in the ultraviolet region has been determined by several workers employing various solvents. The reported spectra are generally in agreement with the one determined in this investigation. The absorption curve is shown in Figure 3 and is compared with those of the cobalt(II) and cobalt(III) complexes. The following table gives values of the molar absorbancy index and the corresponding wavelengths. The values reported by Csaszar and Horvath³⁶ were measured in 98 percent ethanol. Roberts and Field³⁷ and Yamasaki, Hara, and Yasuda³⁸ reported shoulders which appear at 290, 310, and 325 millimicrons; this is in agreement with the present work.

λ m μ	molar absorbancy index	λ m μ	molar absorbancy index	λ m μ	molar absorbancy index	ref.
199	2.45×10^4	227	4.13×10^4	264	3.0×10^4	this work
				265	3.0×10^4	39
		227	3.6×10^4	265	2.6×10^4	38
		228	4.36×10^4	268	2.88×10^4	36

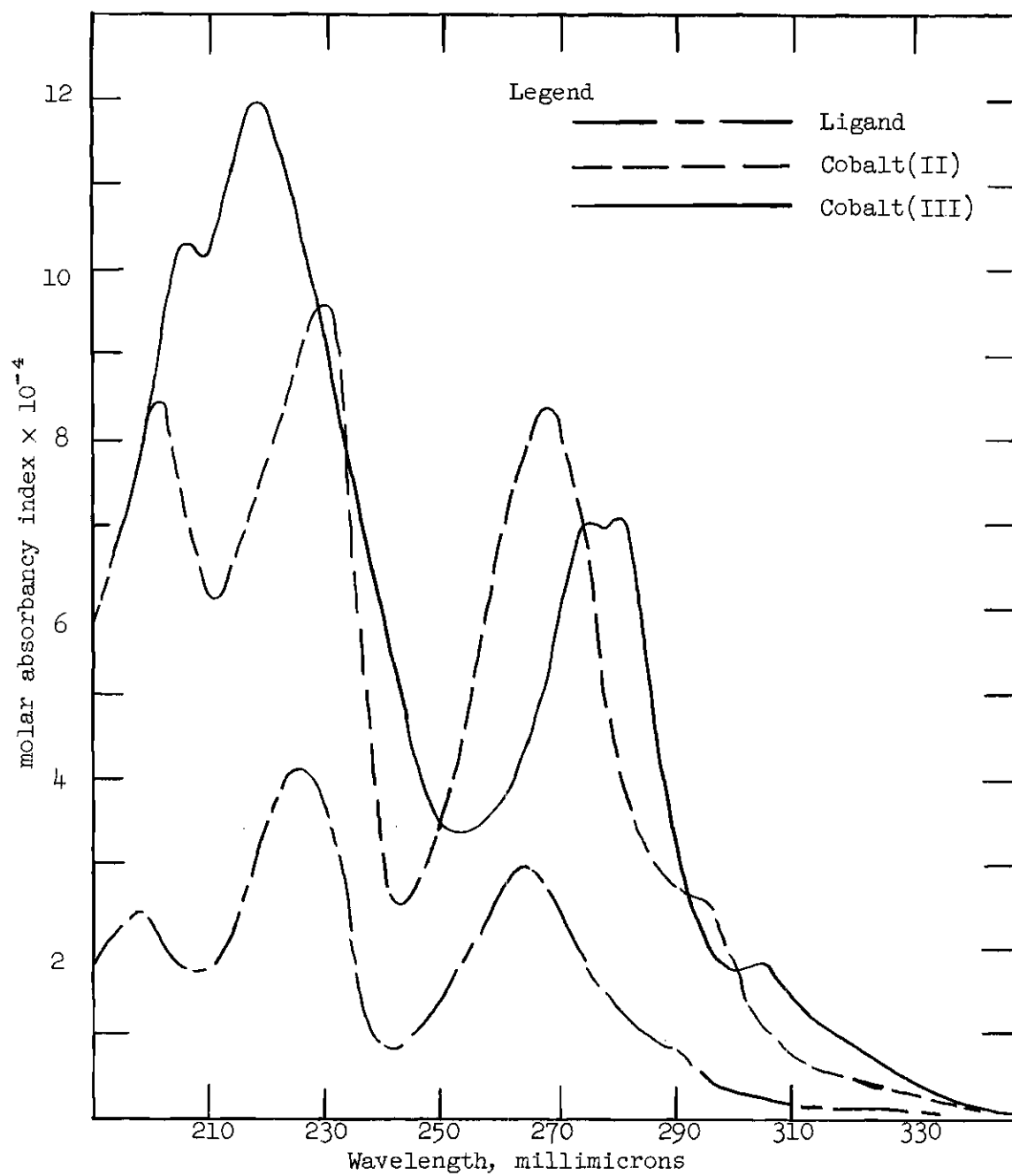


Figure 3. Ultraviolet Absorption Spectra of 1,10-phenanthroline and the Corresponding Tris- Complexes of Cobalt(II) and Cobalt(III)

Tris(1,10-phenanthroline)cobalt(II) Ion. Tris(1,10-phenanthroline)-cobalt(II) ion has been studied in the ultraviolet region by several investigators and the results are not in good agreement. The values reported for wavelengths agree, but the values of molar absorbcancy index differ widely. The spectrum determined in this investigation is reported in Figure 3. The following table displays the data reported by various investigators. Shoulders have been reported at 290, 304, 313, 331, and 348 millimicrons.³⁷

λ m μ	molar absorbancy index	λ m μ	molar absorbancy index	λ m μ	molar absorbancy index	ref.
200	8.5×10^4	227	9.85×10^4	268	8.4×10^4	this work
				267	9.0×10^4	39
		228	1.20×10^5	269	9.5×10^4	38
		228	8.52×10^4	268	6.9×10^4	36

The discrepancy in the values of the molar absorbcancy index may be due to the uncertainty in the number of molecules of water of hydration associated with the complexes. Also, the work of Csaszar and Horvath was conducted in 98 percent ethanol.

The tris(1,10-phenanthroline)cobalt(II) ion is labile and, of course, dissociation to lower complexes and phenanthroline occurs. Consequently, the spectrum is not solely that of the tris species but is a composite.

Tris(1,10-phenanthroline)cobalt(III) Ion. The ultraviolet spectrum has been reported by others^{38, 39} and a serious discrepancy exists. The spectrum determined in this investigation is shown in Figure 3, and com-

pared to the spectra of the corresponding cobalt(II) complex and the ligand. A comparison with values reported by previous investigations is shown in the following table. The value reported at 305 millimicrons is a shoulder that is almost an isolated peak.

λ m μ	molar absorbancy index	λ m μ	molar absorbancy index	λ m μ	molar absorbancy index	ref.
218	1.20×10^5	281	7.10×10^4	305	1.90×10^4	this work
		282	7.10×10^4	305	1.90×10^4	39
220	7.9×10^4	273	5.0×10^4			38

The values of molar absorbancy index and wavelength reported by Baker,³⁹ as well as the general shape of the absorption curve, are in excellent agreement with the one determined in the present investigation. The values of the molar absorbancy index and wavelength and the general shape of the absorption curve reported by Yamasaki, Hara, and Yasuda³⁸ differ rather markedly from those of the present work and are considered to be in error.

Visible and Near Infrared Spectra of 1,10-Phenanthroline and the Corresponding Tris- Cobalt(II) and Cobalt(III) Complexes

1,10-Phenanthroline. The spectrum in the range 550-1150 millimicrons was determined. No peaks occur in this region, but a value of molar absorbancy index of 0.20 or less was noted for the entire region.

Tris(1,10-phenanthroline)cobalt(II) Ion. The spectrum in the region 550-1150 millimicrons was determined employing solutions which were prepared in situ and contained an excess of phenanthroline to insure complete

complexation of the cobaltous ion in the tris form. The excess ligand does not absorb strongly in this region, and the spectrum is considered to represent only the tris(1,10-phenanthroline)cobalt(II) ion. Spectra determined employing water and 50 percent ethanol as solvent are comparable. The alcoholic medium was employed because it is a better solvent for the substituted phenanthrolines studied. Thus, a comparison of the cobaltous complexes employing the various phenanthrolines could be made in the same medium. The spectra in 50 percent ethanol is presented in Figure 4.

The only previously reported data for this region were determined by Csaszar and Horvath.³⁶ The following table offers a comparison:

wavelength millimicrons	molar absorbancy index	solvent	reference
910	6.78	water	this work
910	6.90	50% ethanol	this work
1010	30.2	98% ethanol	36

The results of Csaszar and Horvath differ widely from those obtained in the present investigation; however, the conditions were different and possibly account for the results. The spectra reported in the present investigation were determined in an aqueous medium or in 50 percent ethanol, but the values listed by Csaszar and Horvath were determined in 98 percent ethanol. These investigators did not employ an excess of the ligand to insure complete complexation of the cobaltous ion in the tris form. Consequently, the spectrum they report may not represent the tris(1,10-phenanthroline)cobalt(II) ion, but a composite containing lower complexes

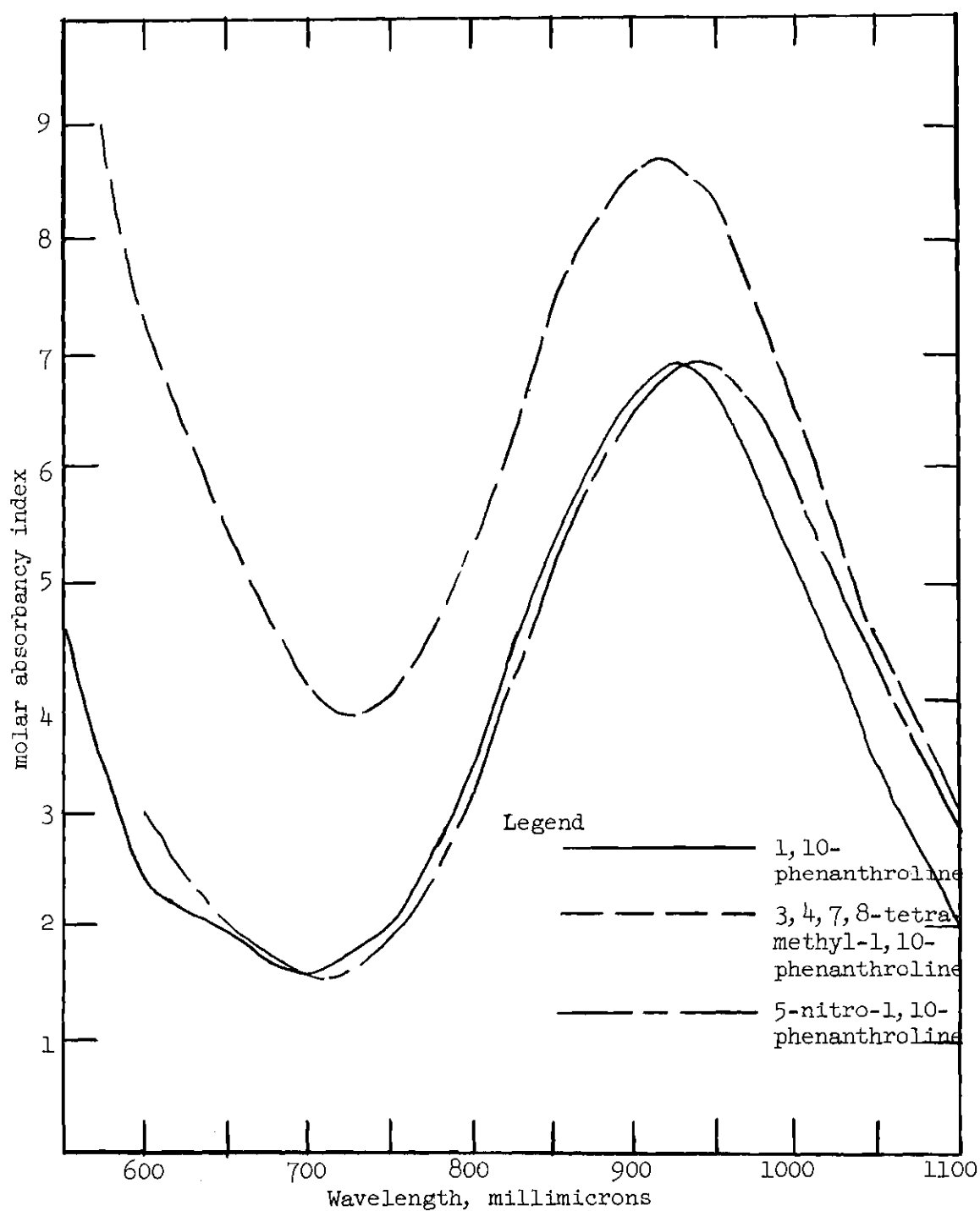


Figure 4. Visible and Near Infrared Absorption Spectra of the Tris-Cobalt(II) Complexes of 1,10-phenanthroline, 5-Nitro-1,10-phenanthroline, and 3,4,7,8-Tetramethyl-1,10-phenanthroline

and oxidation products. Also, since the values of molar absorbancy index reported by these investigators for the ultraviolet region are much smaller than others recorded, their work is believed to be in error.

Tris(1,10-phenanthroline)cobalt(III) Ion. The spectrum of tris(1,10-phenanthroline)cobalt(III) ion was determined in the region 400-1150 millimicrons. There are no isolated peaks in this region; however, there are shoulders which appear in the vicinity of 470 and 720 millimicrons. The shoulders are resolvable by the method of Cook and Neumann.⁴⁰ A plot of log of molar absorbancy index versus wavelength is shown in Figure 5. If the absorbancy is due only to a tail from a large ultraviolet peak, the plot should be linear. Non-linearity is an indication that a peak in this region is hidden under the tail. The linear portion is subtracted and a symmetrical curve remains. This curve is represented by the broken line plot in Figure 5. An absorbance maximum at 470 millimicrons with a molar absorbancy index of 42 is obtained. A similar resolution yields an absorbance maximum at 710 millimicrons with an absorbancy index of 1.10.

Yamasaki, Hara, and Yasuda³⁸ have reported an isolated peak at 451 millimicrons with a molar absorbancy index of 306. This peak did not exist in the spectrum determined in the present investigation. Data reported for this compound in the ultraviolet region by these investigators did not agree with the present work or the work recorded by Baker.³⁹ Consequently, the spectra reported for the tris(1,10-phenanthroline)cobalt(III) ion by these workers must be questioned.

Ultraviolet Spectra of 3,4,7,8-tetramethyl-1,10-phenanthroline and the Corresponding Tris Complexes of Cobalt(II) and Cobalt(III)

Spectra of these compounds have not been recorded in the literature.

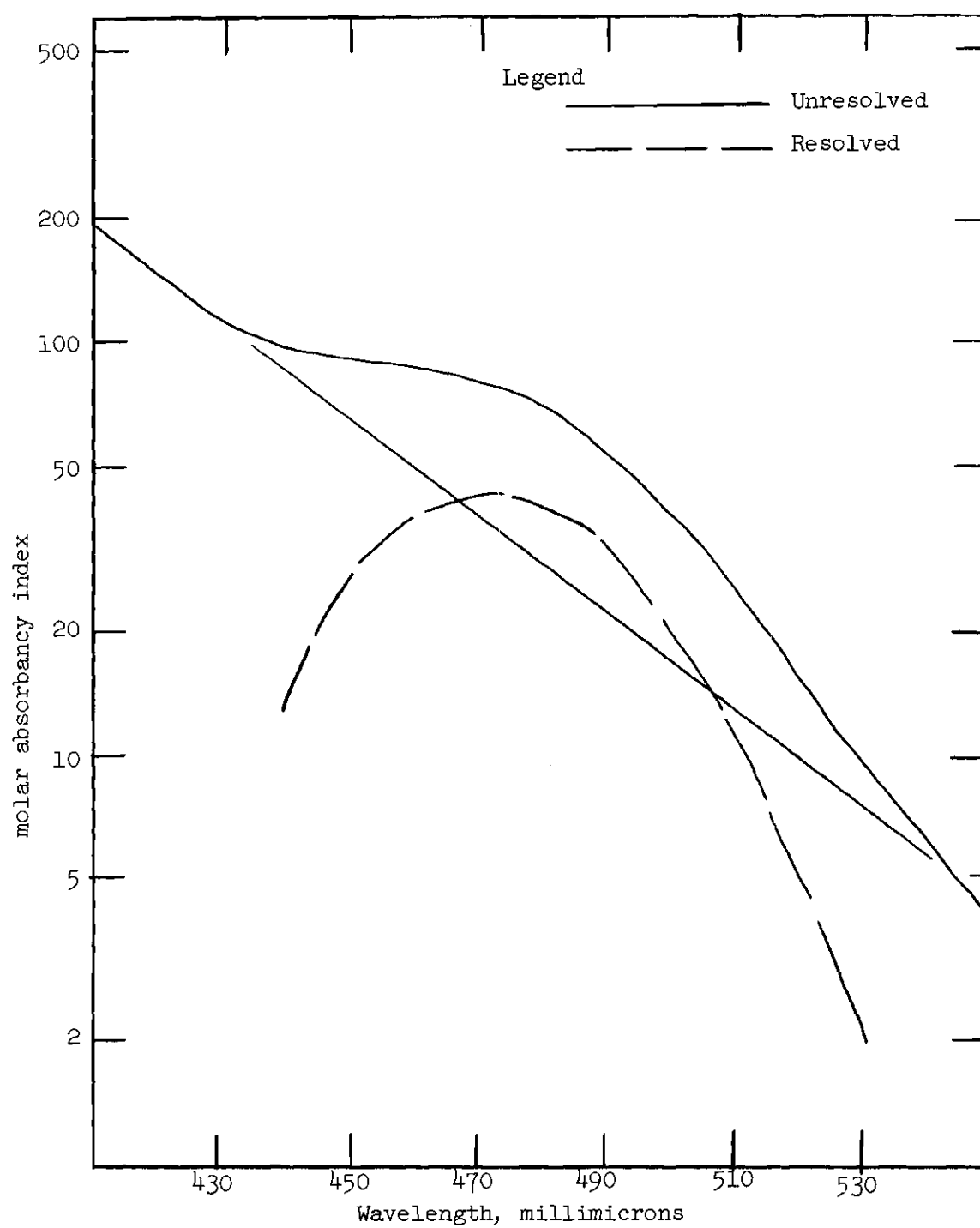


Figure 5. Visible Absorption Spectrum of Tris(1,10-phenanthroline)-cobalt(III)

The spectra determined in the present investigation are presented in Figure 6. The similarity of the spectra of these compounds and the spectra of the corresponding compounds containing 1,10-phenanthroline should be noted.

Visible and Near Infrared Spectra of 3,4,7,8-tetramethyl-1,10-phenanthroline and the Corresponding Tris Complexes of Cobalt(II) and Cobalt(III)

Spectra of these compounds have not been recorded in the literature.

3,4,7,8-Tetramethyl-1,10-phenanthroline. The spectrum in this region was determined in 50 percent ethanol. No peaks were present, but a molar absorptancy index of 0.20 or less was noted for the entire range.

Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(II) Ion. The spectrum was determined employing an excess of ligand in 50 percent ethanol. The spectrum is recorded in Figure 4.

Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III) Ion. The spectrum was determined in aqueous medium. No peaks exist in the region 400-1150 millimicrons; however, shoulders appear in the vicinity of 470 and 750 millimicrons and can be resolved by the method described for tris(1,10-phenanthroline)cobalt(III) ion. The resolution yields a symmetric curve with a molar absorptancy index of 26.8 at 480 millimicrons. The spectrum in the vicinity of 750 millimicrons is more difficult to resolve, but a value of molar absorptancy index of approximately 1.25 was obtained at 750 millimicrons.

Ultraviolet Spectra of 5-nitro-1,10-phenanthroline and the Corresponding Tris Complexes of Cobalt(II) and Cobalt(III)

Spectra of these compounds have not been recorded in the literature. The spectra determined in the present investigation are presented in Figure 7.

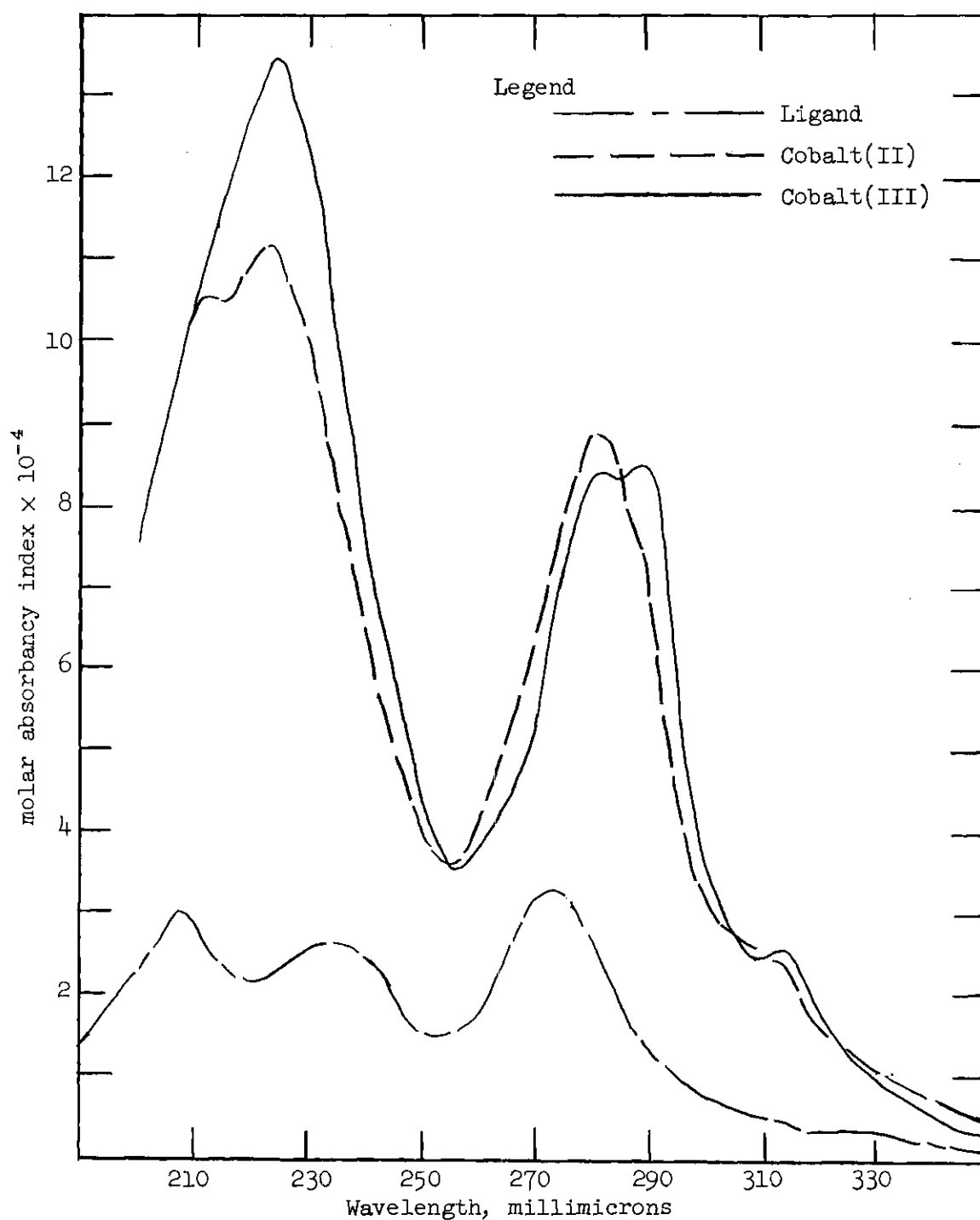


Figure 6. Ultraviolet Absorption Spectra of 3,4,7,8-Tetramethyl-1,10-phenanthroline and the Corresponding Tris- Complexes of Cobalt(II) and Cobalt(III)

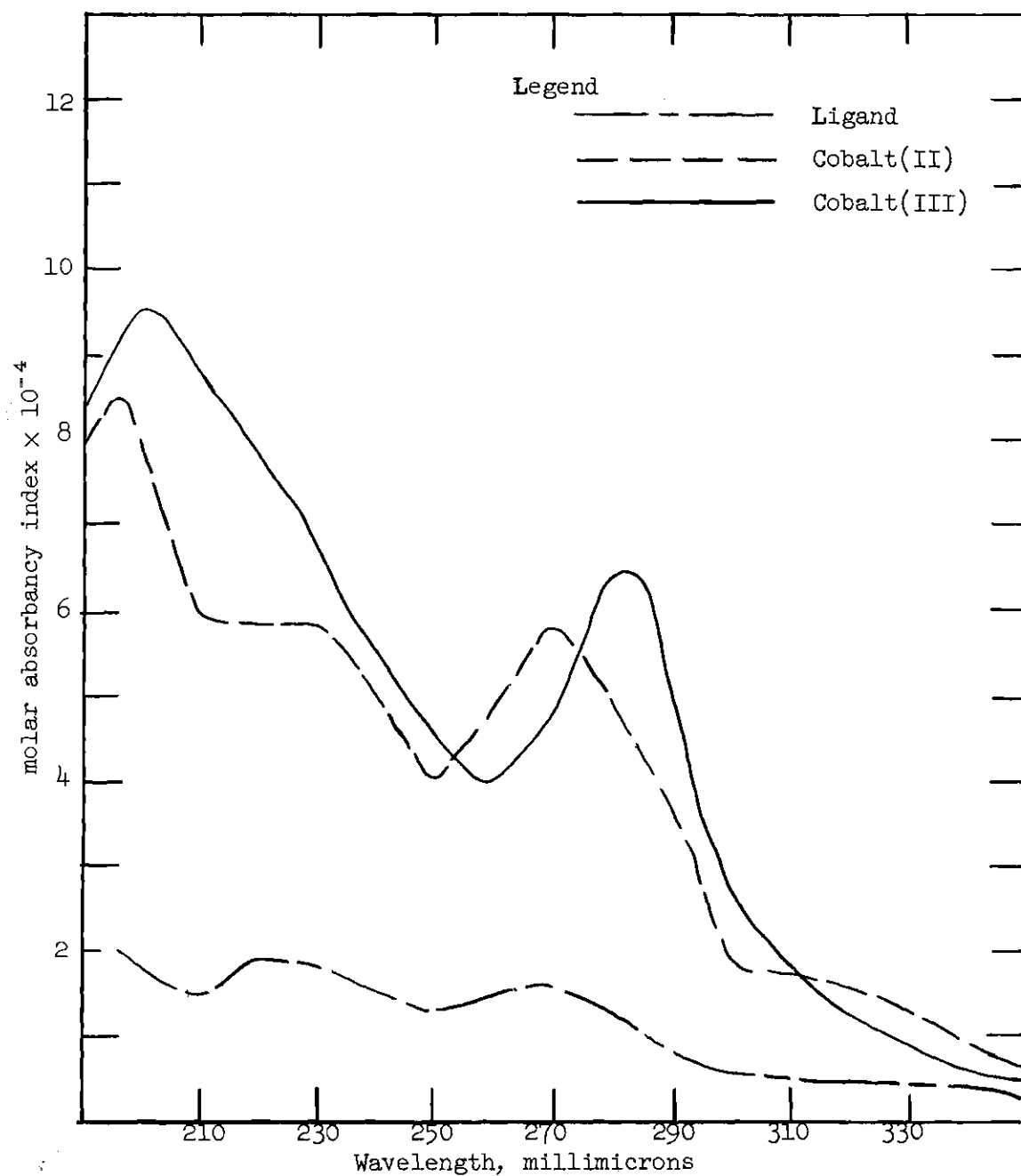


Figure 7. Ultraviolet Absorption Spectra of 5-Nitro-1,10-phenanthroline and the Corresponding Tris- Complexes of Cobalt(II) and Cobalt(III)

Visible and Near Infrared Spectra of 5-nitro-1,10-phenanthroline and the Corresponding Tris Complexes of Cobalt(II) and Cobalt(III)

Spectra of these compounds have not been recorded in the literature.

5-Nitro-1,10-phenanthroline. The spectrum was recorded employing 50 percent ethanol as solvent. No peaks occurred in this region of the spectrum, but a molar absorbancy index of 0.20 or less was noted for the entire region.

Tris(5-nitro-1,10-phenanthroline)cobalt(II) Ion. The spectrum was determined employing 50 percent ethanol as solvent. The spectrum is shown in Figure 4.

Tris(5-nitro-1,10-phenanthroline)cobalt(III) Ion. The spectrum was determined in aqueous medium, no peaks were present in the region 400-1150 millimicrons; however, a shoulder appears in the vicinity of 480 millimicrons and can be resolved by the method previously described. A molar absorbancy index of 32.2 at 480 millimicrons is obtained by the resolution.

Resolution of Cobalt(III) Phenanthroline Complexes

Resolution of the tris(1,10-phenanthroline)cobalt(III) ion into its enantiomorphic forms was accomplished. When antimonyl tartrate is employed as resolving agent, the less soluble diastereoisomer contains levorotatory tris(1,10-phenanthroline)cobalt(III) ion. The levorotatory isomer has been obtained pure as the perchlorate; however, the more soluble dextrorotatory isomer was not obtained optically pure. The molar rotation of 1-tris(1,10-phenanthroline)cobalt(III) perchlorate dihydrate is -7.14×10^5 at the sodium D line.

An unsuccessful attempt to resolve the tris(1,10-phenanthroline)-cobalt(III) ion appears in the literature.¹³ These investigators employed

an aqueous medium and reported that extensive evaporation was necessary to isolate solids. The use of ethanol to decrease the solubility of the desired diastereoisomer eliminates the necessity of evaporation and plays a key role in the resolution.

Partial resolution of the tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III) ion was achieved. It is interesting to note that the less soluble diastereoisomer is dextrorotatory; the less soluble diastereoisomer of tris(1,10-phenanthroline)cobalt(III) antimonyl tartrate is levorotatory. The largest value of the molar rotation obtained for d-tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III) perchlorate is $+ 2.4 \times 10^5$ and, consequently, the value of the completely resolved material must be larger.

Asymmetric Synthesis of d-Tris(1,10-phenanthroline)cobalt(III) Perchlorate

The successful synthesis of optically active tris(1,10-phenanthroline)-cobalt(III) is probably due to the following sequence of reactions. The optically active antimonyl tartrate ion precipitates with only one of the enantiomorphous forms of tris(1,10-phenanthroline)cobalt(II). The latter ion is labile, however, and racemization of the ions remaining in solution occurs, followed by further precipitation with the antimonyl tartrate. In this way, a high yield of one stereoisomeric form is obtained, and configuration is retained in the solid crystalline lattice. In the oxidation step, the configuration of the complex is undoubtedly retained, but the optical purity of the final product will be diminished to the extent that racemization of the cobalt(II) complex occurs in the slurry before oxidation can be accomplished. The observed specific rotation of $+ 367^\circ$ for the tris(1,10-phenanthroline)cobalt(III) perchlorate dihydrate prepared by this method compared with a specific rotation of $+ 765^\circ$ for the completely re-

solved compound indicates that 74 percent of the complex in the final product was in the dextrorotatory form.

Improvement in the conversion may be attainable if a thorough study of oxidation methods and concentration conditions is conducted. Note that the asymmetric synthesis leads to the dextrorotatory cobalt(III) complex while the levorotatory isomer is more easily obtained in the resolution method.

Optical Rotatory Dispersion

Optical rotatory dispersion of l-tris(1,10-phenanthroline)cobalt(III) perchlorate dihydrate was measured and is reported in Figure 8. The dispersion curve was measured for the partially resolved dextrorotatory isomer and was found to have the same shape as the curve for the levorotatory isomer, but, of course, it is inverted.

Optical rotatory dispersion was measured for the partially resolved d-tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(III) ion; this curve is similar in every respect to the curve reported for d-tris(1,10-phenanthroline)cobalt(III) perchlorate.

Magnetic Susceptibility

Magnetic susceptibilities of tris(1,10-phenanthroline)cobalt(II) perchlorate and the corresponding cobalt(II) complexes employing 3,4,7,8-tetramethyl-1,10-phenanthroline and 5-nitro-1,10-phenanthroline were determined by the Gouy method employing $\text{Hg}[\text{Co}(\text{SCN})_4]$ as standard. The specific susceptibility of the standard at 20° C is 16.44×10^{-6} c.g.s. units.

Specific susceptibilities are calculated from the following expression:

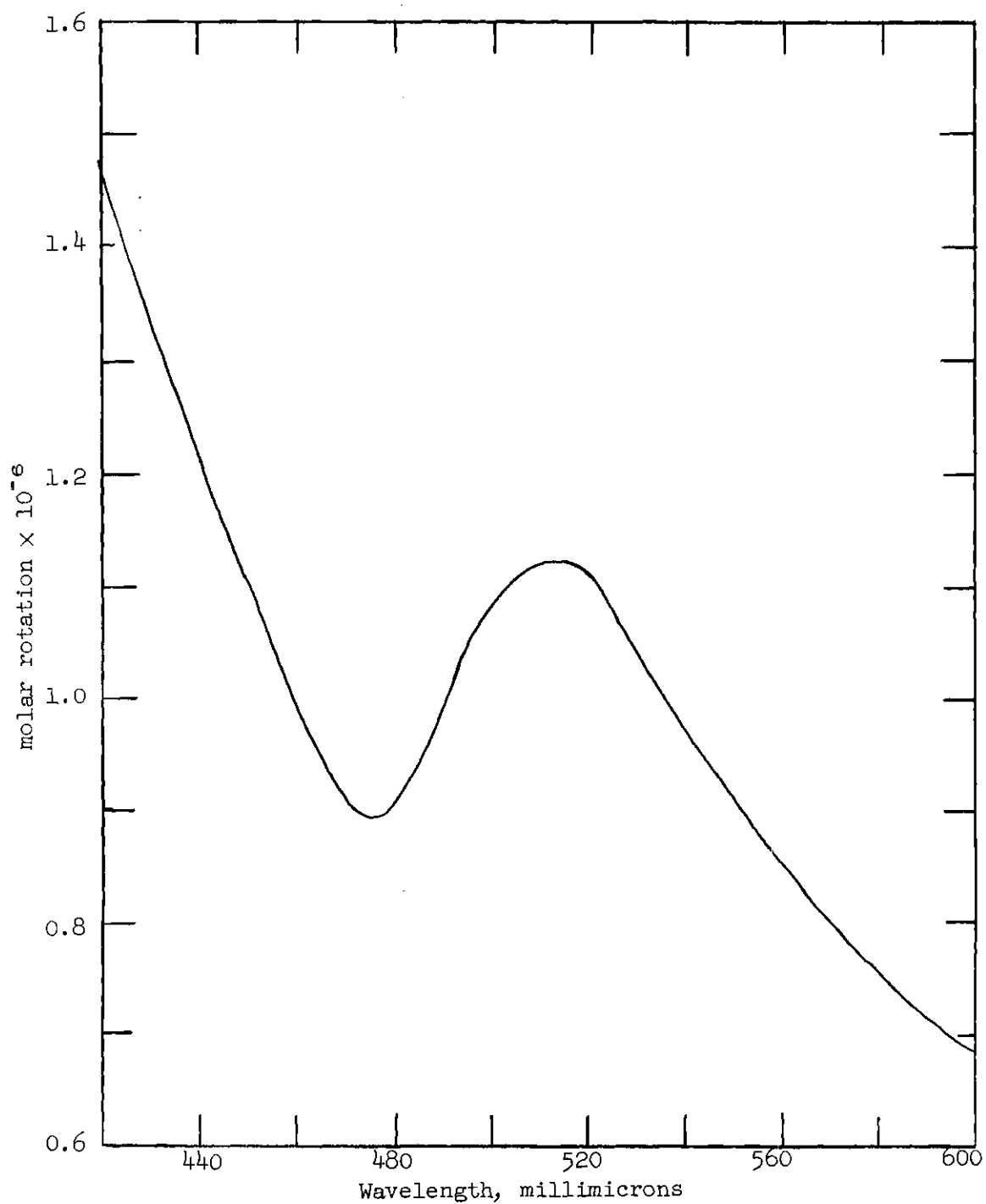


Figure 8. Optical Rotatory Dispersion of 1-Tris(1,10-phenanthroline)-cobalt(III)perchlorate Dihydrate

$$10^6 X = \frac{\alpha + \beta F'}{w}$$

where X = specific susceptibility

α = constant for displacement of air, milligrams

β = tube calibration constant

F' = force on the specimen, milligrams

w = weight of specimen, grams

The tube calibration constant, β , was calculated employing the data in Table 2, the susceptibility of the standard, and $\alpha = 0.037$ milligrams calculated from the volume of the tube, 1.27 ml, and the volume susceptibility of air, $+ 0.029 \times 10^{-6}$ c.g.s. units per cc. The force on the specimen must be corrected to allow for diamagnetism of the Gouy tube; a correction of 6.95 milligrams is necessary. The tube calibration constant is 0.274.

The following table lists the calculated values of specific susceptibility, molar susceptibility, corrected molar susceptibility, and magnetic moments:

Compound	X	X_m	X'_m	μ_{eff}
tris(1,10-phenanthroline)-cobalt(II) perchlorate	12.47×10^{-6}	9.95×10^{-3}	1.04×10^{-2}	5.00
tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(II) perchlorate	8.39×10^{-6}	8.10×10^{-3}	8.70×10^{-3}	4.57
tris(5-nitro-1,10-phenanthroline)cobalt(II) perchlorate	9.91×10^{-6}	9.25×10^{-3}	9.71×10^{-3}	4.83

Molar susceptibilities were corrected for diamagnetism of the ligands and the anions present. Values of 128×10^{-6} and 32×10^{-6} c.g.s. units were employed for 1,10-phenanthroline and perchlorate ion, respectively.⁴¹ Values for 3,4,7,8-tetramethyl-1,10-phenanthroline and 5-nitro-1,10-phenanthroline were estimated to be 176×10^{-6} and 139×10^{-6} c.g.s. units, respectively. Magnetic moments are calculated by the following equation:

$$\mu_{\text{eff}} = 2.84(TX'_m)^{1/2}$$

where T = absolute temperature

X'_m = corrected molar susceptibility

μ_{eff} = effective magnetic moment

Several workers have studied the magnetic property of tris(1,10-phenanthroline)cobalt(II) ion. The following table contains their results:

anion	μ_{eff}	reference
perchlorate monohydrate	5.2	13
perchlorate dihydrate	4.61	27
perchlorate	4.70	42
bromide dihydrate	5.15	43
bromide	5.10	44
chloride trihydrate	4.36	43

The magnetic properties of tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(II) ion and tris(5-nitro-1,10-phenanthroline)cobalt(II) ion ap-

parently have not been studied previously. Pure samples of these compounds are difficult to obtain, since excess ligand frequently precipitates with the desired complex and is extremely difficult to remove. Also, tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(II) ion is easily oxidized; partial oxidation would result in a low value of the magnetic moment.

Treatment of Data for Electron Transfer Reactions

Isotopic Exchange

General. In 1938 McKay⁴⁵ derived an equation which describes the kinetic behavior in a homogeneous isotopic exchange experiment. Since no net chemical change occurs in such a system, the concentrations of the chemical species undergoing exchange are unaltered. Consequently, the rate of exchange between the chemical species is constant. The McKay relationship is valid regardless of the mechanism by which the exchange occurs. The equation is:

$$\ln \left| \frac{A - A_{\infty}}{A_0 - A_{\infty}} \right| = - R \left(\frac{a + b}{ab} \right) t$$

where A_0 = activity of a particular species at zero time

A = activity of a particular species at time t

A_{∞} = activity of a particular species at isotopic equilibrium or infinite time

t = time

R = constant rate of exchange of the two species

a = concentration of one of the exchanging species

b = concentration of the other exchanging species

Some qualifying comments are necessary for the general applicability of this relationship. The equation is valid for molecules which contain only one isotopic exchanging atom; however, if a molecule contains two or more non-equivalent isotopic atoms, the relationship is valid provided all isotopic atoms except one are inert to exchange. If there is more than one equivalent isotopic atom per molecule, the equation is valid provided that concentrations are expressed in units of exchanging atoms and not in molecules. The systems studied in the present research contain only one equivalent isotopic atom per molecule and the above qualifications are not necessary. The McKay equation is applicable in the strictest sense only if complete separation of exchanging species is achieved. In this case, A_0 can be related to the zero time or "separation induced exchange." Frequently the separation procedure employed accelerates the exchange reaction. This acceleration is believed to be caused by such factors as changing the atmosphere of the system during an extraction separation or by surface effects if a precipitation separation is utilized. This exchange is referred to as "separation induced exchange." Wahl and Bonner⁴⁶ have shown the general applicability of the equation when incomplete separation of exchanging species occurs. Kinetic parameters are unaltered, but the separation induced term is changed.

A plot of $\ln(A - A_\infty)$ versus time produces a straight line with slope of $-R(\frac{a+b}{ab})$. The rate of exchange, R , can be evaluated from the slope provided the concentrations of the exchanging species are known. A typical plot is shown in Figure 9.

Isotopic exchange data for the system tris(1,10-phenanthroline)-

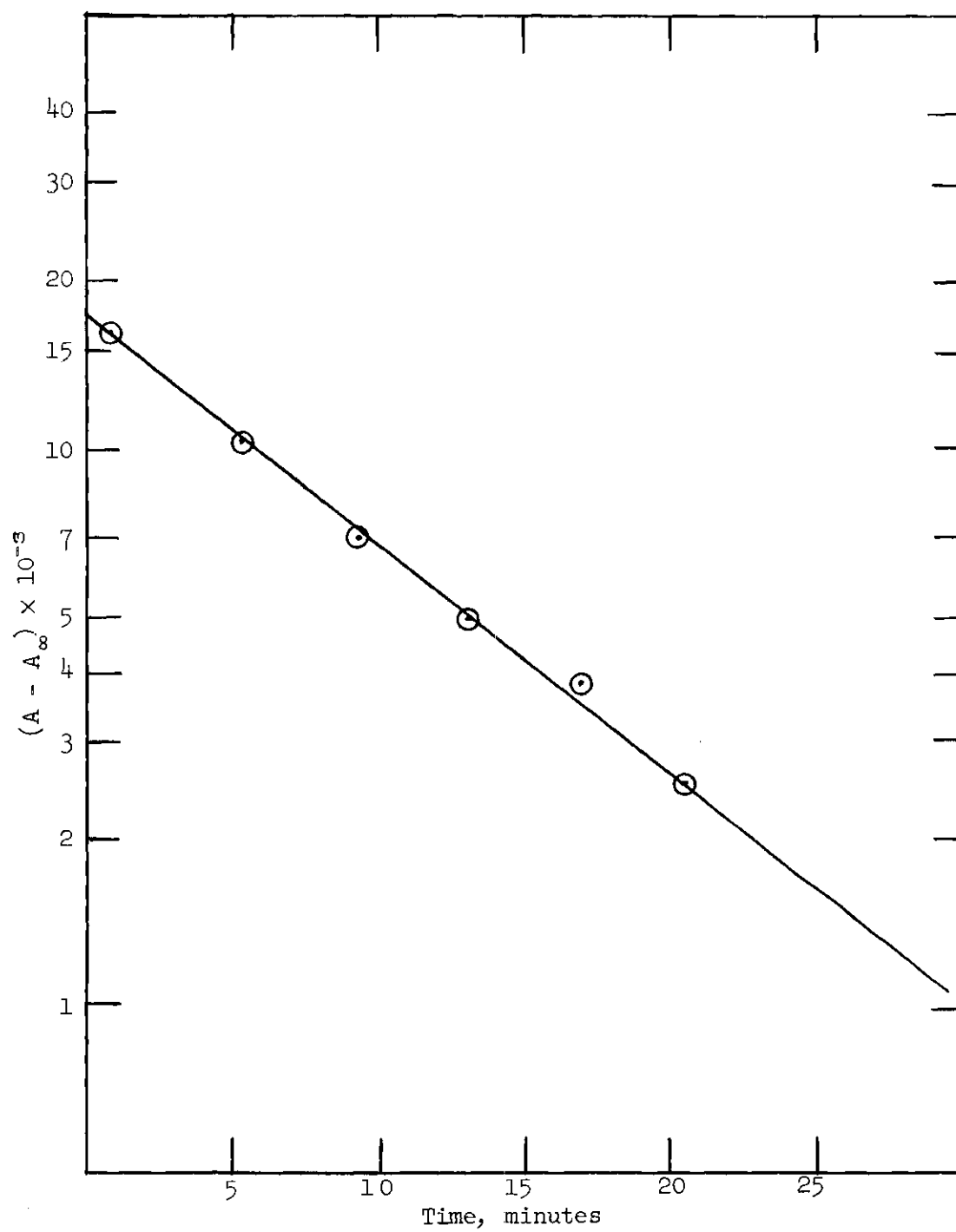


Figure 9. A Typical McKay Plot

cobalt(II) ion, tris(1,10-phenanthroline)cobalt(III) ion are contained in Table 3.

Order of Reaction. R is empirically related to the concentrations of exchanging species by a rate law of the form:

$$R = k[a]^m[b]^n$$

where k is the specific rate constant, and m and n are the order of the reaction in a and b, respectively.

To determine m, the values of R may be evaluated in a series of reactions in which all conditions remain constant except the concentration of a. A plot of log R versus log a yields a straight line of slope m. Similarly, a series of reactions in which b is the only variable will allow the determination of n.

Data from Table 3 are plotted in Figures 10 and 11 to give the dependence of R on the concentrations of tris(1,10-phenanthroline)cobalt(II) ion and tris(1,10-phenanthroline)cobalt(III) ion, respectively. The values obtained are 0.49 for cobalt(II) and 0.76 for cobalt(III) in an ionic atmosphere of 0.01 M KNO_3 . The value for cobalt(III) in an ionic atmosphere of 0.01 M KClO_4 is 0.78. The dotted lines in Figures 10 and 11 indicate that the data may be fitted by a non-linear curve. The slope increases with increasing concentration.

Even though the data are fitted nicely with non-integral orders, the mechanistic explanation of these values is obscure. The values obtained in the present work are between zero and one, and suggest that a rate law of the following form may be operative.

Table 3. Isotopic Exchange Data for the System Tris(1,10-phenanthroline)cobalt(II)-
Tris(1,10-phenanthroline)cobalt(III) at 15° C

Run	Cobalt(II), M	Cobalt(III), M	Slope, min ⁻¹	R × 10 ⁷ min ⁻¹ M	*k × 10 ³	t _{1/2} min
1	3.64 × 10 ⁻⁴	7.27 × 10 ⁻⁶	8.15 × 10 ⁻²	5.80	3.60	8.50
2	1.82 × 10 ⁻⁴	7.27 × 10 ⁻⁶	4.72 × 10 ⁻²	3.29	2.94	14.50
3	9.10 × 10 ⁻⁵	7.27 × 10 ⁻⁶	4.20 × 10 ⁻²	2.84	3.61	16.67
4	4.55 × 10 ⁻⁵	7.27 × 10 ⁻⁶	3.29 × 10 ⁻²	2.08	3.74	21.00
5	1.92 × 10 ⁻⁵	7.12 × 10 ⁻⁴	9.71 × 10 ⁻²	18.16	1.56	7.10
6	1.92 × 10 ⁻⁵	3.63 × 10 ⁻⁴	4.94 × 10 ⁻²	9.01	1.28	14.00
7	1.92 × 10 ⁻⁵	1.68 × 10 ⁻⁴	3.04 × 10 ⁻²	5.24	1.33	23.00
8	1.92 × 10 ⁻⁵	8.71 × 10 ⁻⁵	2.70 × 10 ⁻²	3.46	1.45	31.45
9	1.92 × 10 ⁻⁵	7.12 × 10 ⁻⁴	1.86 × 10 ⁻¹	34.8		3.67
10	1.92 × 10 ⁻⁵	3.63 × 10 ⁻⁴	1.00 × 10 ⁻¹	18.2		6.92
11	1.92 × 10 ⁻⁵	1.68 × 10 ⁻⁴	6.05 × 10 ⁻²	10.6		11.50
12	1.92 × 10 ⁻⁵	8.71 × 10 ⁻⁵	4.08 × 10 ⁻²	6.45		17.08

Runs 1-8 conducted in 0.01 M KNO₃

Runs 9-12 conducted in 0.01 M KClO₄

*k calculated from rate law $R = k[\text{Co(II)}]^{.49}[\text{Co(III)}]^{.76}$

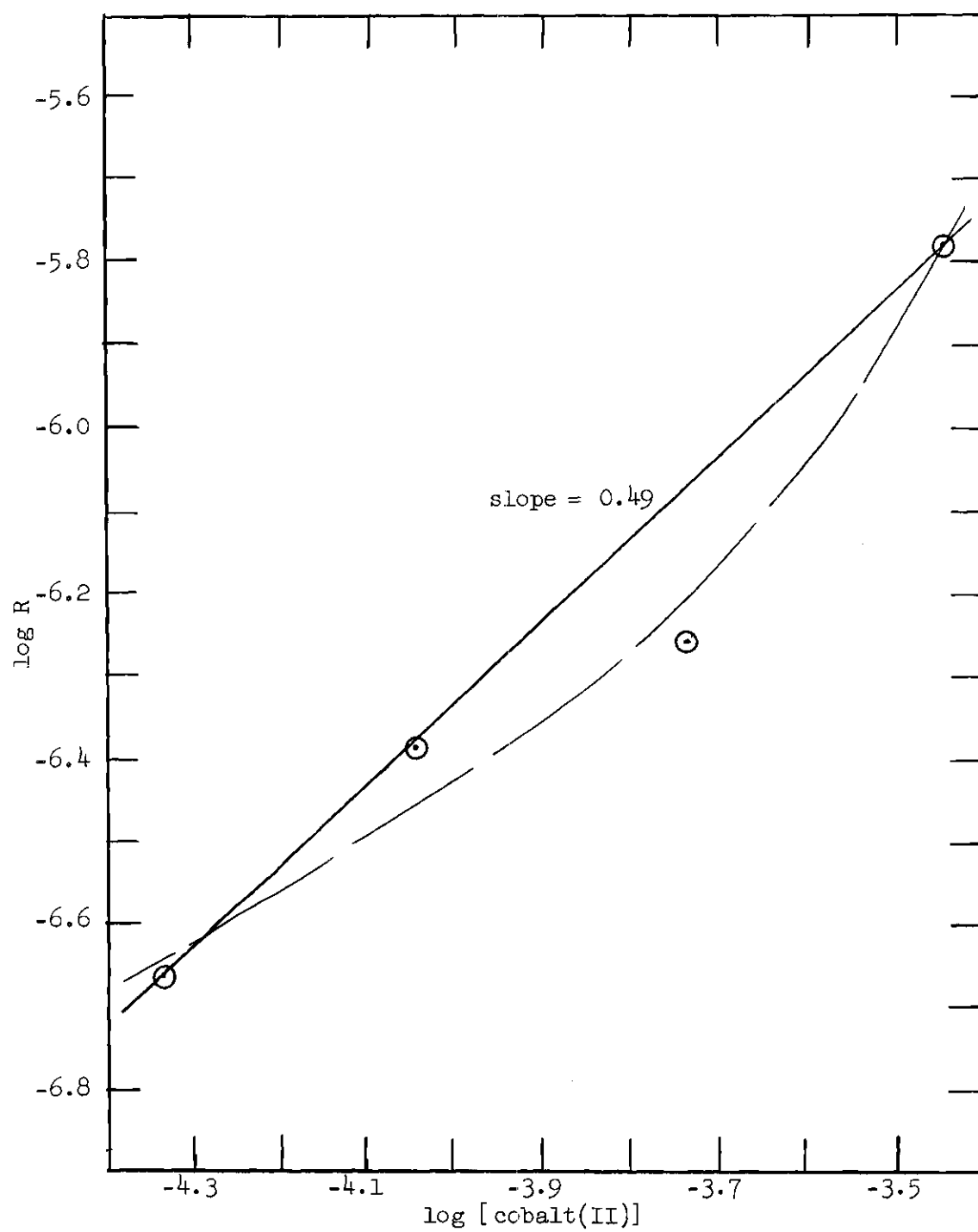


Figure 10. Dependence of Rate on Cobalt(II) by Radioactive Exchange

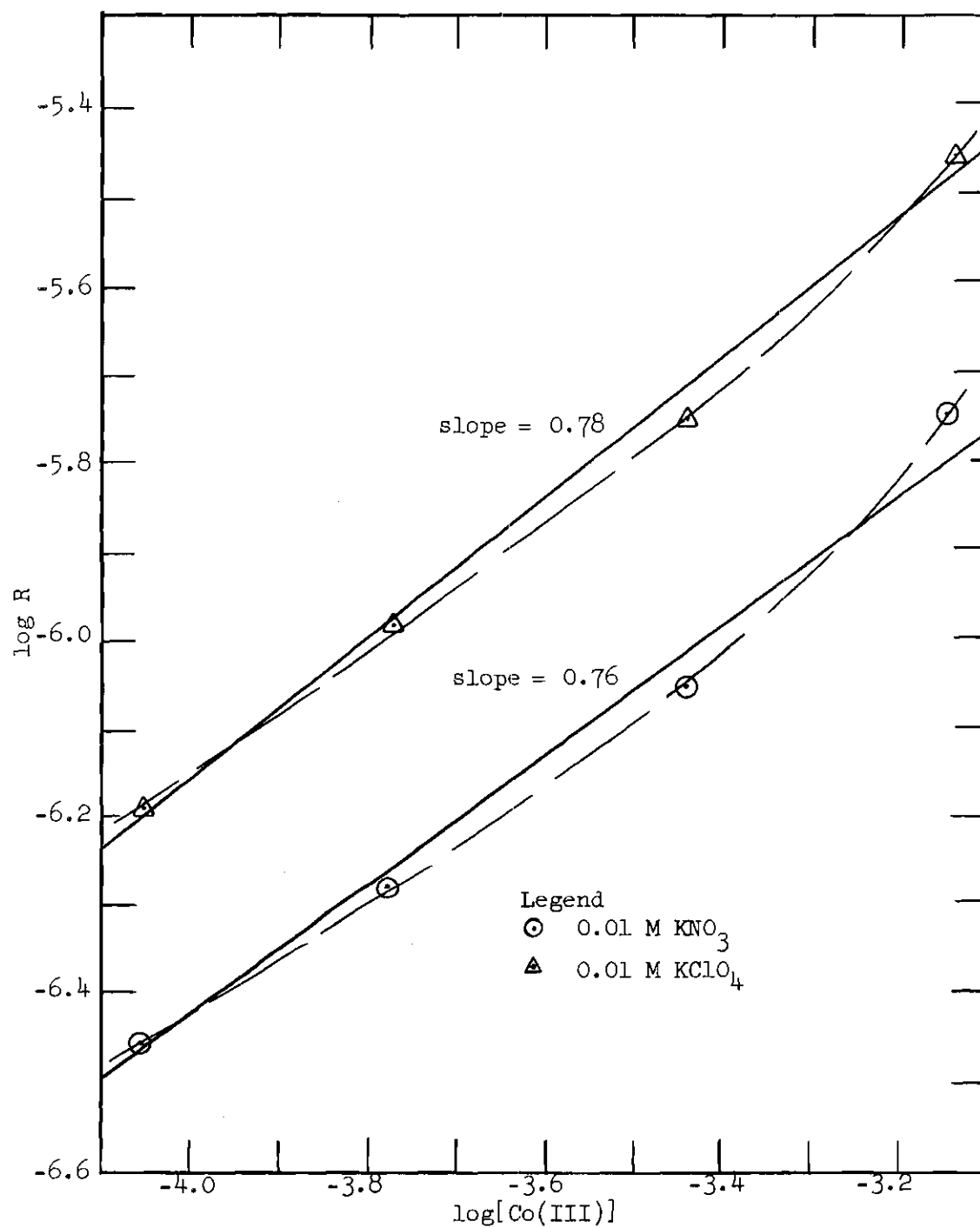


Figure 11. Dependence of Rate on Cobalt(III) by Radioactive Exchange

$$R = k_1[\text{Co(II)}][\text{Co(III)}] + k_2[\text{Co(II)}] + k_3[\text{Co(III)}]$$

If this is the case, $\frac{\text{McKay Slope}}{[\text{Co(II)}] + [\text{Co(III)}]} = K = \frac{R}{[\text{Co(II)}][\text{Co(III)}]}$

and
$$K = k_1 + \frac{k_2}{[\text{Co(III)}]} + \frac{k_3}{[\text{Co(II)}]}$$

In a set of experiments in which cobalt(III) is constant

$$K = \left(k_1 + \frac{k_2}{[\text{Co(III)}]}\right) + \frac{k_3}{[\text{Co(II)}]}$$

If k_2 and k_3 are truly constant, a plot of K versus $\frac{1}{[\text{Co(II)}]}$ should be a straight line of slope k_3 and intercept $\left(k_1 + \frac{k_2}{[\text{Co(III)}]}\right)$.

Similarly, in a set of experiments in which cobalt(II) is constant

$$K = \left(k_1 + \frac{k_3}{[\text{Co(II)}]}\right) + \frac{k_2}{[\text{Co(III)}]}$$

and a plot of K versus $\frac{1}{[\text{Co(III)}]}$ should be a straight line of slope k_2 and

intercept $\left(k_1 + \frac{k_3}{[\text{Co(II)}]}\right)$. Data are collected in Table 4 and plotted in

Figure 12. It should be noted that K is the numerical value that would formally be calculated as the bimolecular rate constant if the reaction is

Table 4. Isotopic Exchange Data for the System Tris(1,10-phenanthroline)cobalt(II)-
Tris(1,10-phenanthroline)cobalt(III) at 15° C.

Run	Cobalt(II)	Cobalt(III)	Cobalt(II) + Cobalt(III)	Slope min ⁻¹	K M ⁻¹ sec ⁻¹	
						<u>1</u>
						[Co(II)]
Set 1 [*] 1	3.64×10^{-4}	7.27×10^{-6}	3.71×10^{-4}	8.15×10^{-2}	3.65	2,650
2	1.82×10^{-4}	7.27×10^{-6}	1.89×10^{-4}	4.77×10^{-2}	4.20	5,550
3	9.10×10^{-5}	7.27×10^{-6}	9.83×10^{-5}	4.20×10^{-2}	7.13	11,000
4	4.55×10^{-5}	7.27×10^{-6}	5.28×10^{-5}	3.29×10^{-2}	10.40	22,000
						<u>1</u>
						[Co(III)]
Set 2 [*] 5	1.92×10^{-5}	7.12×10^{-4}	7.31×10^{-4}	9.71×10^{-2}	2.22	1,405
6	1.92×10^{-5}	3.63×10^{-4}	3.82×10^{-4}	4.94×10^{-2}	2.15	2,750
7	1.92×10^{-5}	1.68×10^{-4}	1.87×10^{-4}	3.04×10^{-2}	2.70	5,950
8	1.92×10^{-5}	8.71×10^{-5}	1.06×10^{-4}	2.70×10^{-2}	4.23	11,480
						<u>1</u>
						[Co(III)]
Set 3 ^{**} 9	1.92×10^{-5}	7.12×10^{-4}	7.31×10^{-4}	1.86×10^{-1}	4.25	1,405
10	1.92×10^{-5}	3.63×10^{-4}	3.82×10^{-4}	1.00×10^{-1}	4.37	2,750
11	1.92×10^{-5}	1.68×10^{-4}	1.87×10^{-4}	6.05×10^{-2}	5.39	5,950
12	1.92×10^{-5}	8.71×10^{-5}	1.06×10^{-4}	4.08×10^{-2}	6.38	11,480

* Sets 1 and 2 were conducted in 0.01 M KNO₃

** Set 3 was conducted in 0.01 M KClO₄

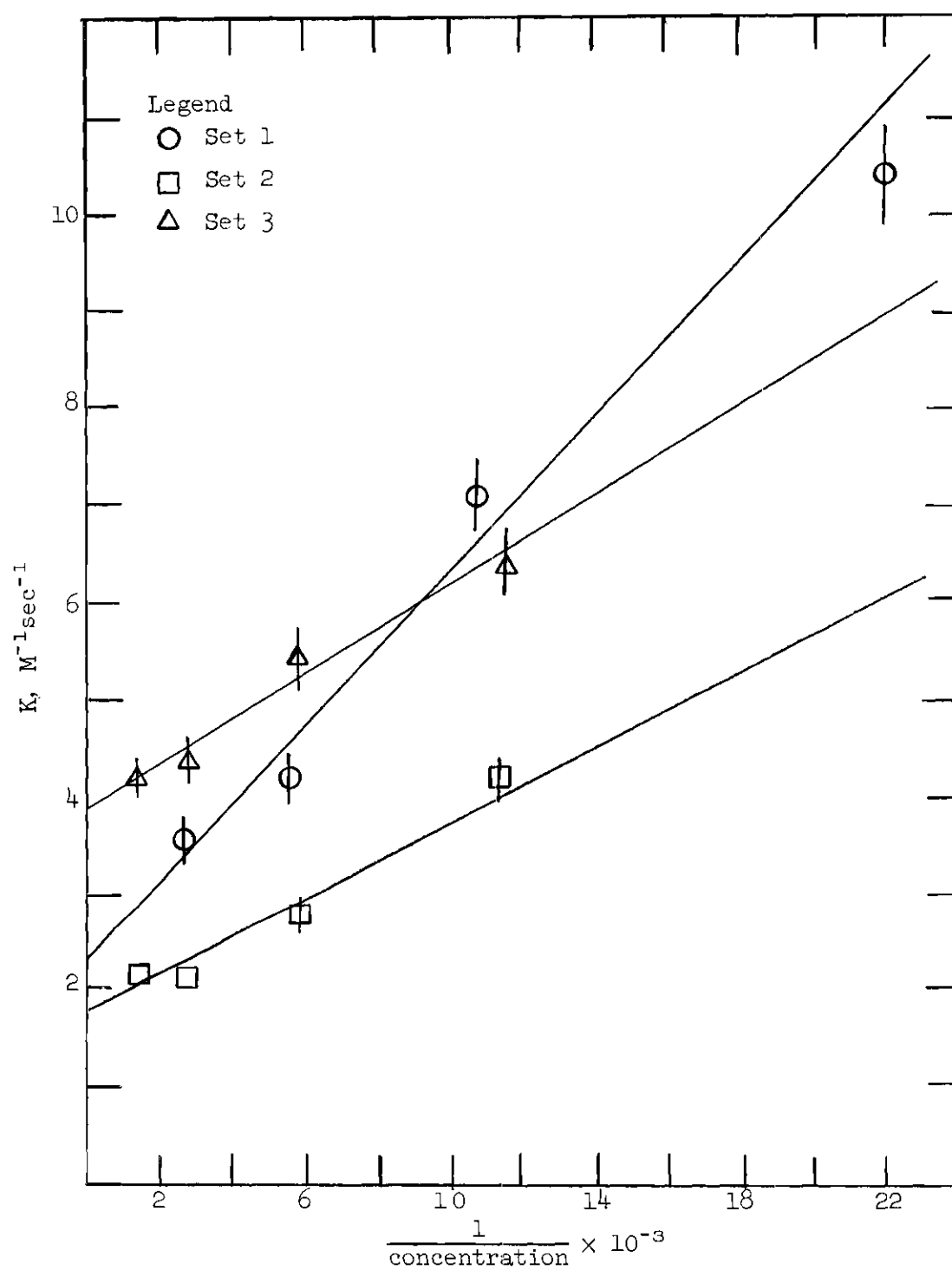
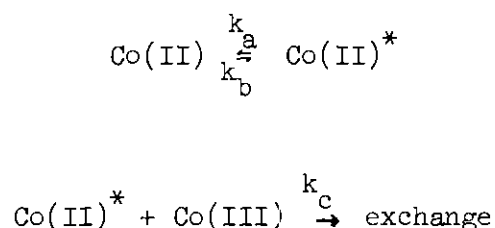


Figure 12. Test of Postulated Rate Law

assumed to proceed purely by a bimolecular path. Comparison of Figure 12 with Figures 10 and 11 shows that the data are fitted as well by this rate law as the one with non-integral exponents.

If k_2 and k_3 are numerical constants, a combination of the values from the two sets of experiments should yield a value of k_1 . Since such a combination yields a negative value of k_1 , it is concluded that k_2 and k_3 are not numerical constants.

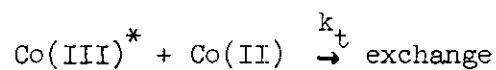
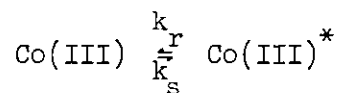
The qualitative behavior of k_2 and k_3 can be rationalized in terms of simple mechanisms. To account for the second term in the rate law, assume a mechanism such as



The species indicated as Co(II)^* might be an excited electronic state of the Co(II) complex ion, or it might be an intermediate resulting from the reaction of a catalytic impurity with the Co(II) ion. Application of the steady-state condition leads to

$$\text{Rate by this path} = \frac{k_a k_c [\text{Co(III)}]}{k_b + k_c [\text{Co(III)}]} [\text{Co(II)}]$$

A similar mechanism is used to account for the third term in the rate law.



$$\text{Rate by this path} = \frac{k_r k_t [\text{Co(II)}]}{k_s + k_t [\text{Co(II)}]} [\text{Co(III)}]$$

Rather than being true constants, k_2 and k_3 then have the form

$$k_2 = \frac{k_a k_c [\text{Co(III)}]}{k_b + k_c [\text{Co(III)}]}$$

$$k_3 = \frac{k_r k_t [\text{Co(II)}]}{k_s + k_t [\text{Co(II)}]}$$

Rigorous testing of this more complicated rate law is not possible because of insufficiency of data. However, it may be noted that:

$$k_2 \rightarrow k_a \quad \text{for large } [\text{Co(III)}]$$

$$k_2 \rightarrow \frac{k_a k_c}{k_b} [\text{Co(III)}] \quad \text{for small } [\text{Co(III)}]$$

$$k_3 \rightarrow k_r \quad \text{for large } [\text{Co(II)}]$$

$$k_3 \rightarrow \frac{k_r k_t}{k_s} [\text{Co(II)}] \quad \text{for small } [\text{Co(II)}]$$

If runs one through four of Table 4 are considered to fit the case of small $[\text{Co(III)}]$ and large $[\text{Co(II)}]$, then

$$K = (k_1 + \frac{k_a k_c}{k_b}) + \frac{k_r}{[\text{Co(II)}]}$$

corresponding to the linearity observed.

If runs five through eight of Table 4 are considered to fit the case of large $[\text{Co(III)}]$ and small $[\text{Co(II)}]$, then

$$K = (k_1 + \frac{k_r k_t}{k_s}) + \frac{k_a}{[\text{Co(III)}]}$$

corresponding to the linearity observed.

The quantity of greatest interest in these experiments is the bimolecular rate constant k_1 . If the mathematical expressions indicated above are valid, the relationship between k_1 and each intercept of Figure 12 is explicit. If the expressions are not valid, the plots may be considered as merely empirical devices for extrapolation of K to infinite concentration, where the reaction must proceed solely by the bimolecular path. It may then be concluded that $k_1 \lesssim 2 \text{ M}^{-1}\text{sec}^{-1}$ in 0.01 M KNO_3 , and $k_1 \lesssim 4 \text{ M}^{-1} \text{ sec}^{-1}$ in 0.01 M KClO_4 at 15° C .

Activation Energy. The energy of activation of a reaction may be determined provided the rate of the reaction is known at several temperatures. The specific rate constant is related empirically to the temperature by the Arrhenius equation,

$$k = A e^{-\frac{E_a}{R'T}}$$

$$\log k = \log A - \frac{E_a}{2.303 R'T}$$

where k = specific rate constant

A = frequency factor

E_a = energy of activation

R' = gas constant

T = absolute temperature

A plot of $\log k$ versus $\frac{1}{T}$ gives a straight line of slope $-\frac{E_a}{2.303 R'}$

from which the activation energy can be evaluated. Since the slope from a McKay plot is directly related to the specific rate constant, a plot of \log McKay slope versus $\frac{1}{T}$ yields a straight line with slope $-\frac{E_a}{2.303 R'}$. Re-

actions were conducted at several temperatures, and in various ionic atmospheres. The data are collected in Table 5 and plotted in Figure 13.

Electron Transfer in the System Tris(5-nitro-1,10-phenanthroline)-Cobalt(II) - Tris(5-nitro-1,10-phenanthroline)Cobalt(III). Attempts were made to study electron transfer in this system by radioactive exchange; however, the results were somewhat unsatisfactory. Successive samples taken at infinite time with respect to the exchange reaction showed increasing activity with time, indicating some net chemical change in the system, and causing some uncertainty in the correct infinite time value. Use of an incorrectly high infinite time value would lead to a calculated

Table 5. Rate of Radioactive Exchange at Various Temperatures in Various Media

Medium	[Co(II)] $\times 10^5$	[Co(III)] $\times 10^4$	Temp. °C	Slope min^{-1}	$t_{1/2}$ min	E_a kcal
No added electrolyte	1.92	3.50	5	1.94×10^{-2}	40.00	8.2 ± 0.6
			15	3.12×10^{-2}	22.50	
			20	3.83×10^{-2}	18.33	
			25	5.24×10^{-2}	13.08	
1.0×10^{-4} M Na_2SO_4	1.92	3.39	5	1.37×10^{-2}	50.75	9.0 ± 0.6
			15	2.55×10^{-2}	27.33	
			20	3.21×10^{-2}	21.84	
			25	4.08×10^{-2}	17.17	
0.01 M Na_2SO_4	1.92	3.60	5	2.47×10^{-2}	28.18	9.9 ± 0.7
			10	3.45×10^{-2}	20.00	
			15	4.15×10^{-2}	16.66	
			20	6.08×10^{-2}	11.33	
			25	8.37×10^{-2}	8.42	
0.01 M KClO_4	1.92	3.63	5	6.61×10^{-2}	10.50	7.7 ± 0.6
			10	8.36×10^{-2}	8.33	
			15	1.00×10^{-1}	6.55	
			20	1.31×10^{-1}	5.33	
			25	1.66×10^{-1}	4.17	
0.01 M KNO_3	1.92	3.63	5	3.04×10^{-2}	22.75	7.4 ± 0.6
			10	4.35×10^{-2}	16.00	
			15	4.94×10^{-2}	14.00	
			20	5.81×10^{-2}	11.84	
			25	7.93×10^{-2}	8.75	

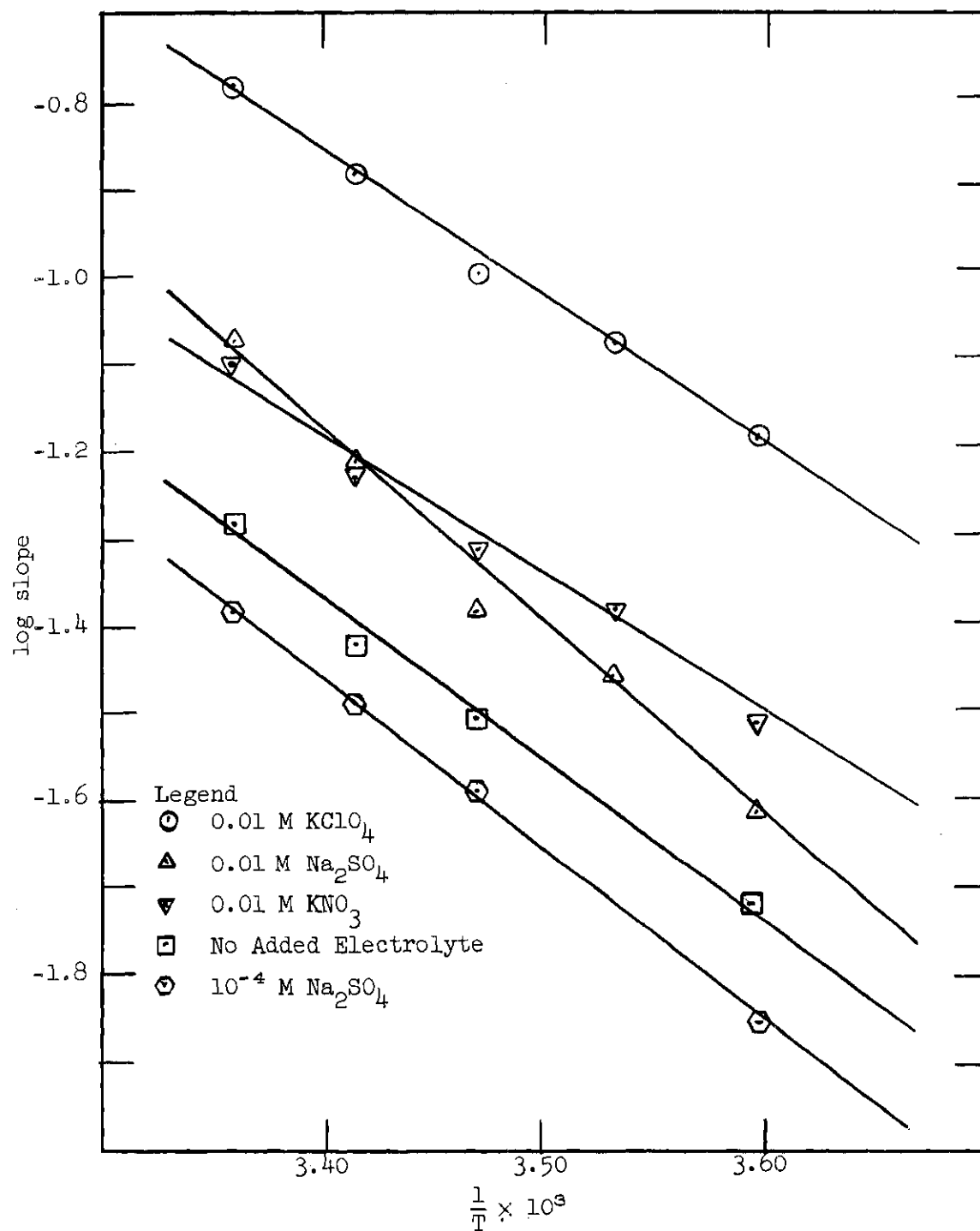


Figure 13. Activation Energy of the System Tris(1,10-phenanthroline)-cobalt(II)-Tris(1,10-phenanthroline)cobalt(III) by Radioactive Exchange

rate that is too high.

In a reaction at 15° C in 0.01 M KNO₃ solution with [Co(II)] = 1.8×10^{-5} and [Co(III)] = 1.73×10^{-4} , the slope of the McKay equation was $2.15 \times 10^{-2} \text{ min}^{-1}$ and the half-time was 32.5 min. If a bimolecular reaction is assumed, a value of $1.13 \text{ M}^{-1} \text{ sec}^{-1}$ for the specific rate constant at 15° C is calculated. Both the uncertainty about the infinite time value and the assumption of a bimolecular reaction make the calculated value an upper limit. A series of reactions was conducted at several temperatures, and a value of 6.1 kcal/mole was obtained for the activation energy.

Racemization

General. In 1950 Dwyer and Gyarfas⁴⁷ suggested that the use of optical activity should provide a technique for studying the rates of electron transfer in suitable systems. Yong Ae Im and Daryle H. Busch⁸ have derived equations relating the change of optical rotation to the rate of electron transfer. These equations were verified by comparing the results obtained by isotopic exchange and the optical activity method for a few selected systems. The expression applicable to the cobalt(II), cobalt(III) phenanthroline systems is derived on the basis that one of the exchanging species is configurationally unstable. The equation is:

$$-\ln\left(\frac{\alpha}{\alpha_0}\right) = \frac{Rt}{[\text{Co(III)}]}$$

where α_0 = rotation at zero time

α = rotation at time t

t = time

R = constant rate of exchange

$[\text{Co(III)}]$ = molar concentration of cobalt(III)

A plot of $\ln(\alpha)$ versus t gives a straight line of slope $\frac{R}{[\text{Co(III)}]}$. Consequently, the rate of exchange, R , can be calculated provided the concentration of cobalt(III) is known. A typical plot is shown in Figure 14.

Electron transfer data studied by the change in optical rotation for the system tris(1,10-phenanthroline)cobalt(II) ion, tris(1,10-phenanthroline)-cobalt(III) ion are contained in Table 6.

Order of Reaction. The rate, R , can be empirically related to the concentrations of the cobalt(II) and cobalt(III) complexes by the following rate law:

$$R = k [\text{Co(II)}]^m [\text{Co(III)}]^n$$

At constant $[\text{Co(III)}]$, a plot of $\log R$ versus $[\text{Co(II)}]$ yields a straight line of slope m . Similarly, a plot of $\log R$ versus $\log [\text{Co(II)}]$ yields a straight line of slope n provided $[\text{Co(III)}]$ remains constant. Such plots are displayed in Figures 15 and 16.

The dependence of the rate on cobalt(II) is 0.94, and the data in Figure 16 for the dependence of cobalt(III) is fitted by a line of slope 1.00. Consequently, within experimental error the reaction is first order in cobalt(II) and first order in cobalt(III), indicating a bimolecular reaction as the predominant mechanism.

Activation Energy. A series of reactions was conducted with the only variable being temperature, so that the activation energy could be

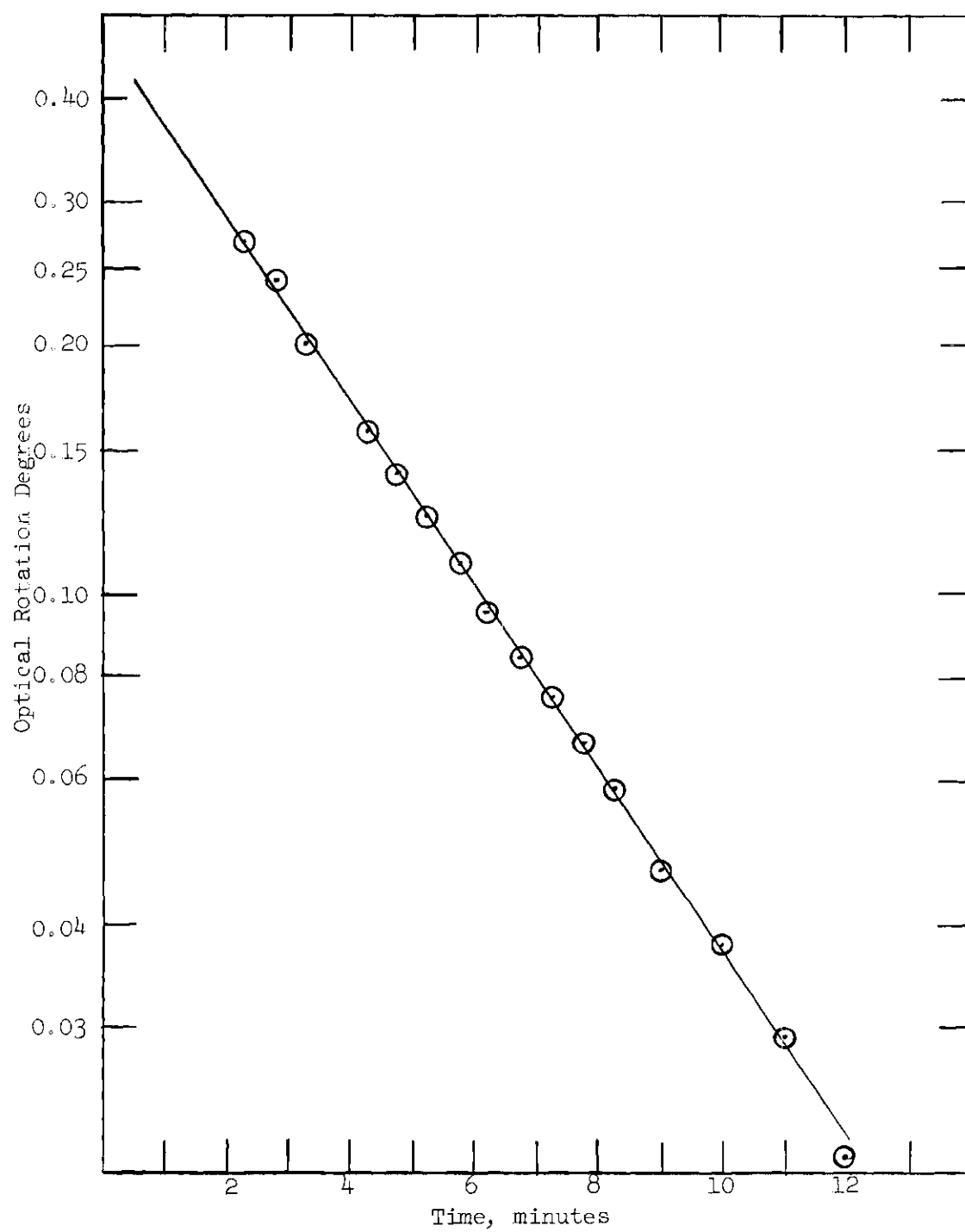


Figure 14. Typical Racemization Plot

Table 6. Racemization Data for the System Tris(1,10-phenanthroline)cobalt(II)-Tris(1,10-phenanthroline)cobalt(III) at 25° C in 0.10 M KNO₃

Run	[Co(II)] × 10 ⁴	[Co(III)] × 10 ⁴	Slope × 10 ¹ min ⁻¹	R × 10 ⁴ M min ⁻¹	k M ⁻¹ sec ⁻¹	t _{1/2} min	pH
1	9.38	4.31	4.27	1.84	7.60	1.62	6.85
2	4.69	4.31	2.66	1.14	9.45	2.65	6.55
3	2.35	4.31	1.30	0.56	9.23	5.25	6.22
4	1.17	4.31	0.70	0.30	9.94	9.90	
5	4.69	9.45	2.53	2.39	9.02	2.75	6.60
6	4.69	4.72	2.59	1.22	9.20	2.50	6.73
7	4.69	4.72	2.11	1.00	7.50	3.25	6.73
8	4.69	2.36	2.16	0.51	7.66	3.75	6.88

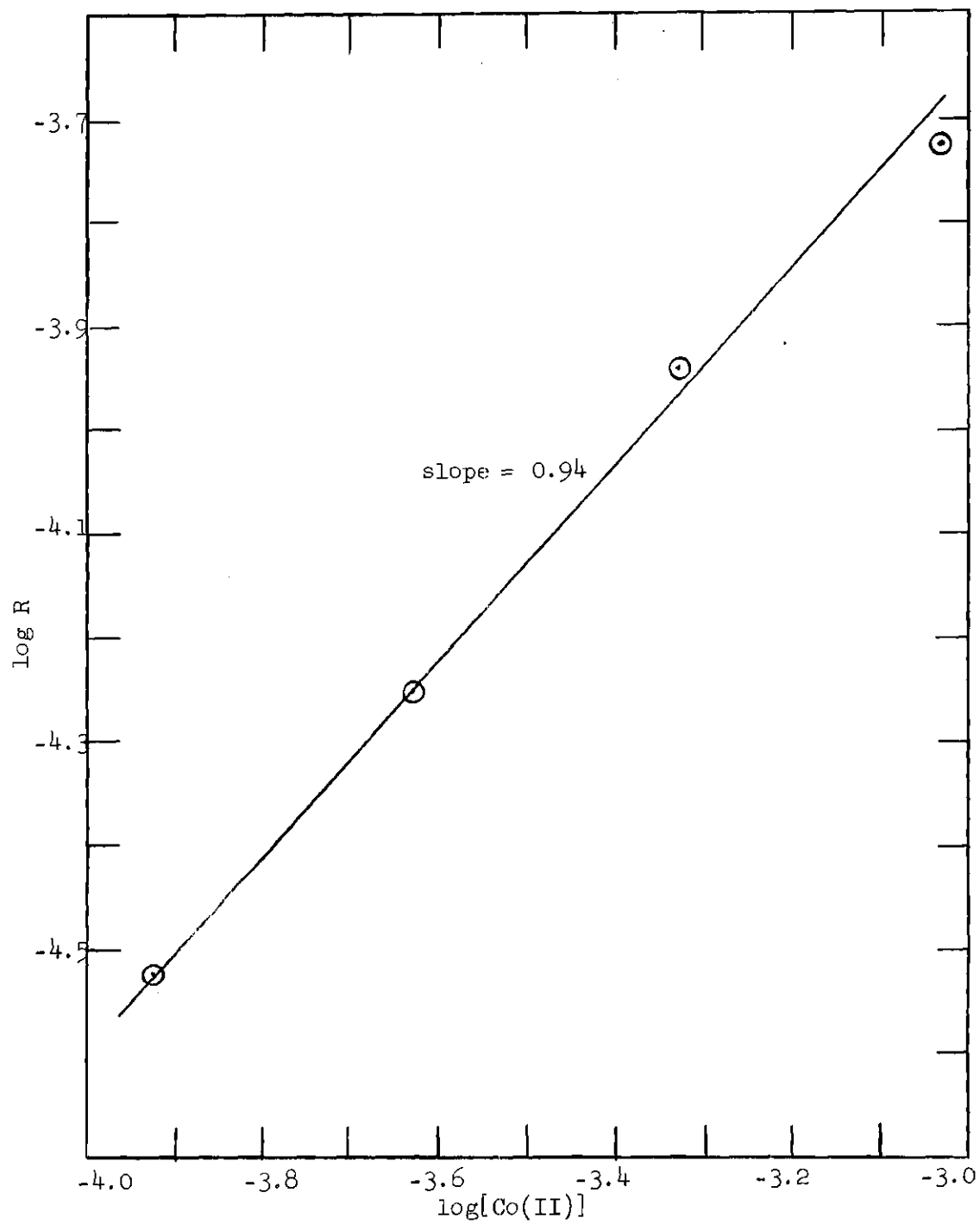


Figure 15. Dependence of Rate on Cobalt(II) by Racemization

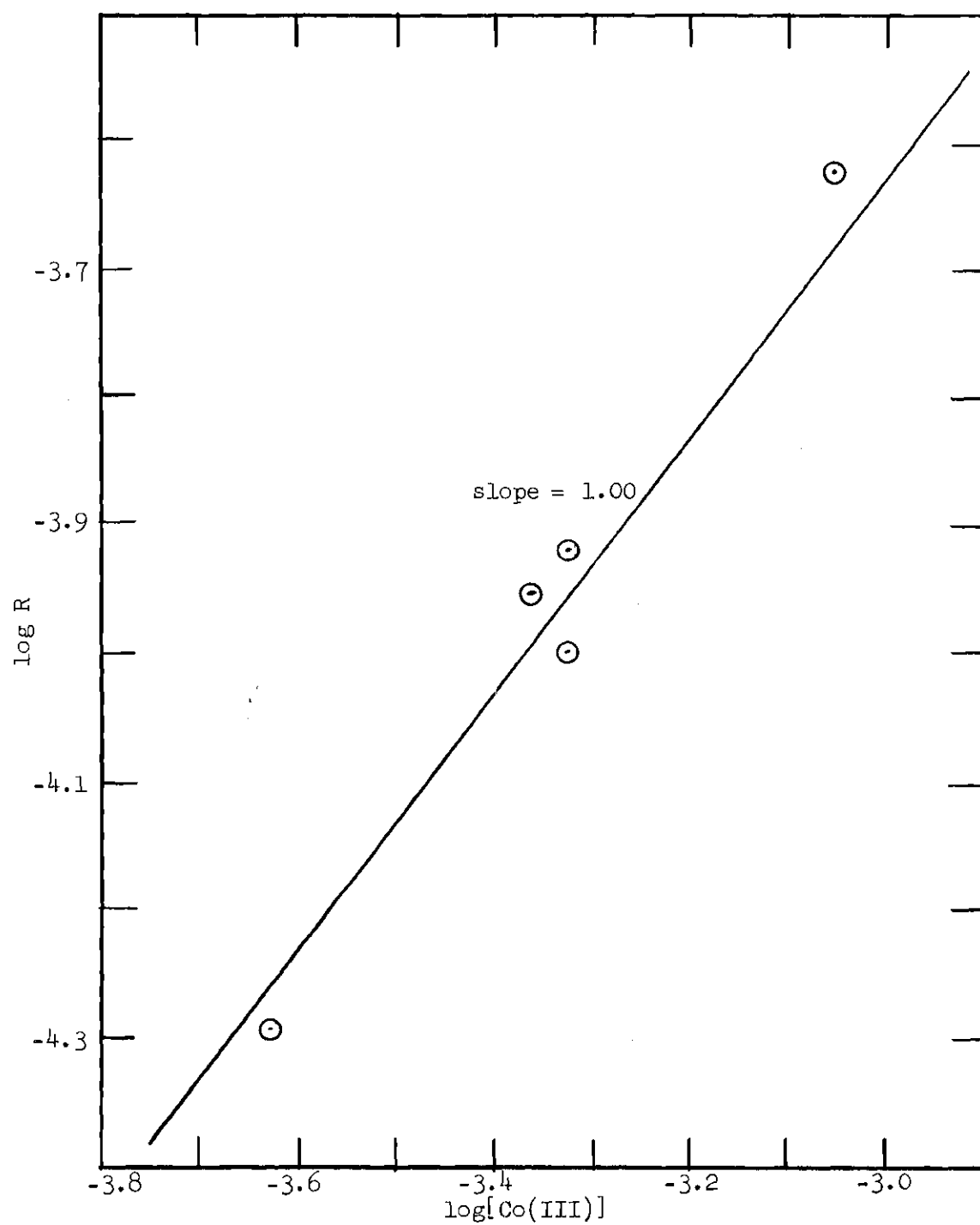


Figure 16. Dependence of Rate on Cobalt(III) by Racemization.

evaluated. The specific rate constant is directly related to the slope of a plot of $\ln(\alpha)$ versus time. Thus, a plot of log slope versus $1/T$ yields a straight line with slope $-\frac{E_a}{2.303 R}$, from which the activation energy, E_a , can be evaluated. Data are contained in Table 7 and plotted in Figure 17. The activation energy is 5.80 kcal.

Entropy of Activation. According to the transition-state theory of chemical kinetics,⁴⁸ the specific rate constant, k , is given by

$$k = \kappa \left(\frac{R'T}{Nh} \right) e^{\frac{\Delta S}{R'}} e^{-\frac{\Delta H}{R'T}}$$

where κ = the transmission coefficient

R' = gas constant

N = Avogadro's number

h = Planck's constant

ΔS = entropy of activation

ΔH = enthalpy of activation

The entropy of activation can be calculated from the above equation only after making certain assumptions. In the absence of evidence to the contrary, the transmission coefficient is generally assumed to be unity.

The quantity ΔH is generally somewhat smaller than the empirical activation energy E_a , but the actual relationship between these quantities is uncertain unless detailed information about the pertinent partition functions is available. Making the assumptions that $\kappa = 1$ and that $\Delta H = E_a$, and using values of $k = 9.45 \text{ M}^{-1} \text{ sec}^{-1}$ and $E_a = 5.80 \text{ kcal per mole at}$

Table 7. Rate of Racemization at Various Temperatures

Run	[Co(II)] $\times 10^4$	[Co(III)] $\times 10^4$	Temp. °C	Slope min^{-1}	$R \times 10^4$ $M \text{ min}^{-1}$	k $M^{-1}\text{sec}^{-1}$	$t_{1/2}$ min
1	4.69	7.83	15	0.179	1.40	6.35	3.85
2	4.69	7.83	25	0.266	2.08	9.45	2.60
3	4.69	7.83	35	0.347	2.72	12.33	2.00

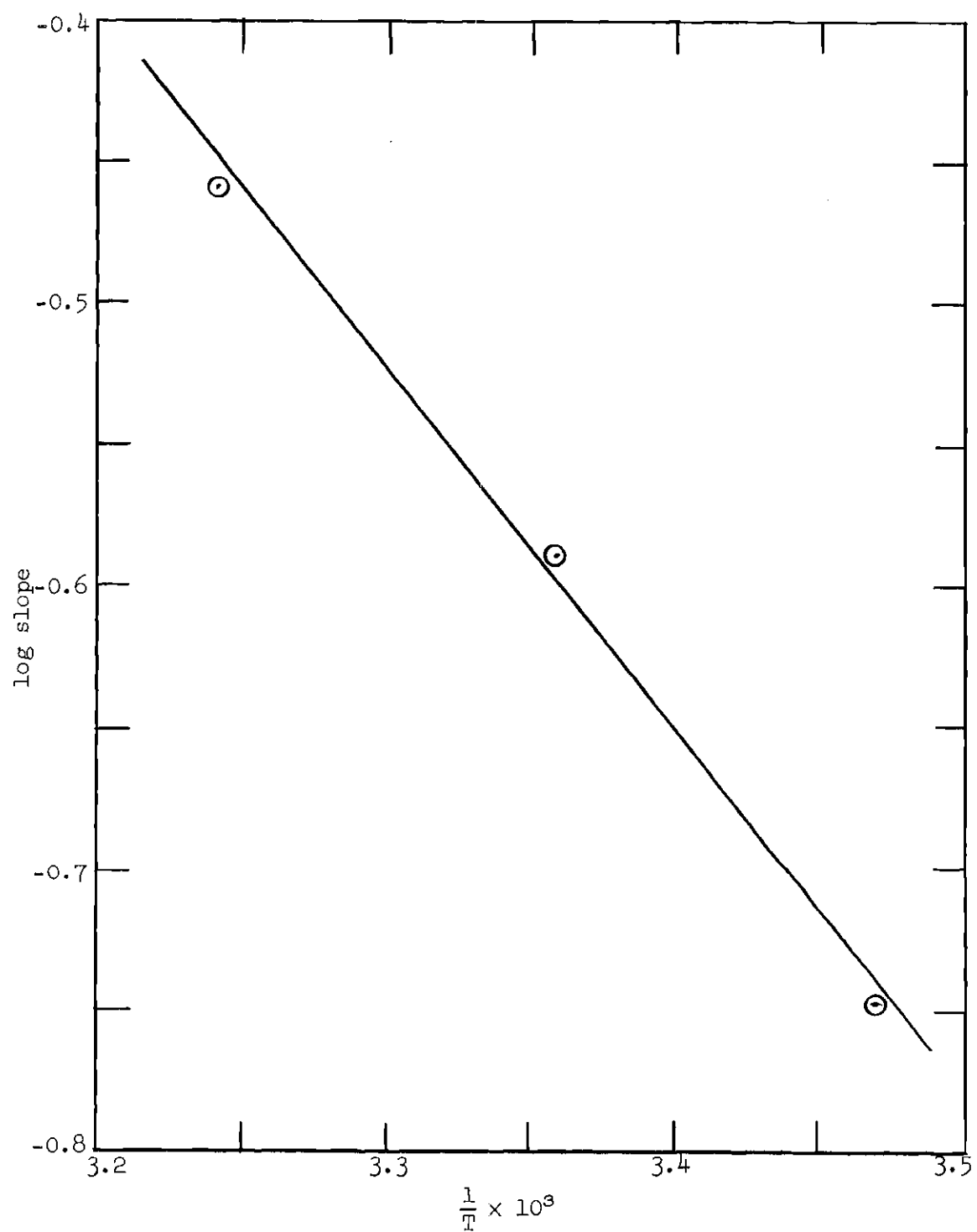


Figure 17. Activation Energy of the System Tris(1,10-phenanthroline)-cobalt(II)-Tris(1,10-phenanthroline)cobalt(III) by Racemization

25° C, gives an entropy of activation of $-35 \text{ cal mole}^{-1} \text{ degrees}^{-1}$.

Electron Transfer in the System Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)cobalt(II) - Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)-cobalt(III). Attempts to study this system completely were unsuccessful; however, a limiting value of the specific rate constant was evaluated. The difficulty encountered in this system is that the ligand is very insoluble in water. Consequently, sufficient excess of ligand cannot be attained, and the cobalt(II) complex apparently oxidizes through a lower complex. If the cobalt(II) complex is partially oxidized, the decrease in its concentration will lead to a slower rate. Thus the reaction which possessed the shortest half-time for comparable conditions was selected to calculate a limiting value of the specific rate constant. The reaction was conducted in 0.10 M KNO_3 solution at 25° C with $[\text{Co(II)}] = 7.5 \times 10^{-5}$ and $[\text{Co(III)}] = 6.45 \times 10^{-4}$. A plot of $\log [\alpha]$ versus t produced a straight line of slope 0.52 min^{-1} and a half-time of 1.33 minutes. If a bimolecular reaction is assumed, a value of $115 \text{ M}^{-1} \text{ sec}^{-1}$ is calculated for the specific rate constant.

CHAPTER IV

CONCLUSIONS

Spectra of 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, and the corresponding tris-complexes of cobalt(II) and cobalt(III) were determined in the region 200-1150 millimicrons. The ultraviolet spectra of the complexes exhibit large molar absorbancy indices (of the order of 10^5), but are essentially the spectra of the ligands slightly perturbed by complexation. The cobalt(II) complexes absorb in the near infrared region in the vicinity of 910 millimicrons with molar absorbancy indices of less than ten. These are ligand field bands and give a measure of the ligand field strengths. The peak of the 3,4,7,8-tetramethyl complex is shifted slightly to shorter wavelengths compared to the unsubstituted complex while the 5-nitro complex is shifted to slightly longer wavelengths. Thus, the ligand field strengths are ordered as the base strengths: 5-nitro-1,10-phenanthroline < 1,10-phenanthroline < 3,4,7,8-tetramethyl-1,10-phenanthroline. The tris-cobalt(III) complexes do not exhibit isolated peaks in the visible or near infrared region, but shoulders appear which are capable of resolution. Resolved peaks are in the vicinity of 470 millimicrons with molar absorbancy indices of 30 to 40.

The tris(1,10-phenanthroline)cobalt(III) complex was successfully resolved into its optical isomers by employing antimonyl tartrate as resolving agent and adding ethanol to decrease the solubility of the less

soluble diastereoisomer. Ellis, Wilkins, and Williams¹³ reported an unsuccessful attempt to resolve this complex using aqueous media. They indicated that solids were not obtained from aqueous media without extensive evaporation, and concluded that exchange and possible racemization in neutral solution prevented resolution. The use of ethanol to decrease the solubility of the diastereoisomer eliminated the necessity of evaporations, and certainly played a significant role in the resolution. A solution of the resolved material does not racemize rapidly, but has a half-time of the order of five to six days at room temperature. Ellis, Wilkins, and Williams prepared the cobalt(III) complex by methods of Pfeiffer and Werdelmann.³¹ Even though analytical data reported by the latter for the cobalt(III) compound are good, other workers using the same preparative method report data for this material which does not agree with the known spectrum of this compound. Consequently, the purity of the tris(1,10-phenanthroline)cobalt(III) utilized in the attempted resolution is questionable.

The optically active tris(1,10-phenanthroline)cobalt(III) was also prepared by an asymmetric synthesis. Antimonyl tartrate preferentially converts the labile tris(1,10-phenanthroline)cobalt(II) to one stereoisomer, which can be oxidized to the inert cobalt(III) complex. Optical rotatory dispersion of the l-tris(1,10-phenanthroline)cobalt(III) complex was measured in the region 420-600 millimicrons, and is consistent with the measured absorption spectrum in the vicinity of 470 millimicrons.

Magnetic susceptibilities of the tris-cobalt(II) complexes of 1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, and 5-nitro-1,10-phenanthroline were measured by the Gouy method. The effective magnetic

moments, calculated from the susceptibility data, are 5.00, 4.57, and 4.83 B.M. respectively. As a result of a theoretical treatment that includes spin-orbit coupling, Figgis and Lewis⁴⁹ conclude that a spin-free octahedral complex of cobalt(II) should have a magnetic moment of about 5.2 at 300° K, or somewhat lower if the symmetry of the ligand field departs from octahedral. They have also tabulated the measured moments reported for 31 complexes generally accepted as having octahedral structures; all but one of the values fall in the range 4.25-5.37. The magnetic measurements on the phenanthroline complexes of cobalt(II) demonstrate that the complexes are spin-free. Of course, the cobalt(III) complexes are spin-paired.

The electron transfer for the system tris(1,10-phenanthroline)-cobalt(II) - tris(1,10-phenanthroline)cobalt(III) was studied by radioactive exchange, as well as by racemization of the optically active cobalt(III) complex. Preliminary experiments indicated that the rate of transfer increased with increasing concentration of excess phenanthroline and then reached a plateau with no further increase in rate. This indicates that exchange occurs more rapidly with the tris-cobalt(II) species than with lower complexes.

The half-time of exchange measured by the racemization method is longer than the half-time measured by radioactive exchange. Consequently, higher concentrations may be employed in the racemization method. In racemization experiments, using concentrations in the range 10^{-3} to 10^{-4} M, the dependence of the rate on [cobalt(II)] and [cobalt(III)] is first order in each.

Concentrations employed in the radioactive exchange studies were in the range 10^{-4} to 10^{-6} M. When the data were analyzed according to the

customary empirical rate law,

$$R = k [\text{Co(II)}]^m [\text{Co(III)}]^n$$

fractional values of m and n were indicated. Even though the data are fitted well by constant fractional values of m and n , mechanistic interpretation is difficult. The same data may be fitted as well by assuming that m and n increase with concentration.

A rate law which can be rationalized in mechanistic terms is the following:

$$R = k_1[\text{Co(II)}][\text{Co(III)}] + k_2[\text{Co(II)}] + k_3[\text{Co(III)}]$$

where k_2 is a function of Co(III) only and k_3 is a function of Co(II) only. At sufficiently high concentrations, the bimolecular reaction appears to be the predominant one. This conclusion is based on the results of the racemization experiments, and the fact that the first term in the rate law becomes relatively more important as the concentrations increase. The value of the specific rate constant at infinite concentration is considered to be the bimolecular constant. The unimolecular terms cannot be given a mechanistic interpretation; they may represent true unimolecular paths of reaction, or may be pseudo first-order paths involving catalysts.

The activation energy of the exchange reaction was determined by radioactive exchange, as well as by the racemization procedure. The values are listed below for various media.

Medium	Method	Activation Energy, kcal
No added electrolyte	Radioactive exchange	8.2 ± 0.6
1.0×10^{-4} M Na_2SO_4	Radioactive exchange	9.0 ± 0.6
0.01 M Na_2SO_4	Radioactive exchange	9.9 ± 0.7
0.01 M KNO_3	Radioactive exchange	7.4 ± 0.6
0.01 M KClO_4	Radioactive exchange	7.7 ± 0.6
0.10 M KNO_3	Racemization	5.8 ± 0.5

These values are lower than the value of 17 ± 5 reported by Baker¹⁴ for no added electrolyte. His specific rate constants are greater than those obtained in this work, suggesting that in his experiments a large fraction of reaction was proceeding by catalytic paths. He prepared the cobalt(III) complex by bromine oxidation. Preliminary experiments indicated that this preparative method might lead to erroneous results and could account for the high rates reported by Baker.

A value of -35 cal per degree-mole was obtained for the entropy of activation employing the activation energy determined by the racemization process.

The rate of reaction is noted to increase with increasing concentration of inert electrolyte. This is expected for reactions between ions of like charge. Specific salt effects were noted in the study of activation energy and are displayed in Figure 13. The rates in 0.01 M Na_2SO_4 and in 0.01 M KNO_3 are comparable, but the rate in 0.01 M KClO_4 is greater by a factor of two. It is interesting to note that the rate in 1.0×10^{-4} M Na_2SO_4 is slightly slower than the rate with no added electrolyte; however,

the rate in 0.01 M Na_2SO_4 is 1.5 times as fast as with no added electrolyte. Baker noted a similar behavior with KCl.

The limited solubility of 5-nitro-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline in water would not allow sufficient excess ligand for complete complexation of the cobalt(II) species. If a sufficient excess of ligand is not available, dissociation occurs and oxidation of the bis species results. Solutions containing two moles of ligand per mole of metal ion have been shown to air oxidize extremely readily. Sufficient data were collected to report limiting values of the rate. The data are collected in the following table to allow comparison with the system utilizing unsubstituted phenanthroline as ligand:

Ligand	Medium	Method	k	Temp. °C
1,10-phenanthroline	0.01 M KNO_3	Radioactive	1.82	15
1,10-phenanthroline	0.01 M KClO_4	Radioactive	3.92	15
5-nitro-1,10-phenanthroline	0.01 M KNO_3	Radioactive	1.13	15
1,10-phenanthroline	0.10 M KNO_3	Racemization	6.35	15
1,10-phenanthroline	0.10 M KNO_3	Racemization	9.45	25
3,4,7,8-tetramethyl-1,10-phenanthroline	0.10 M KNO_3	Racemization	115.	25

Even though an insufficiency of data will not allow a comparison of the three systems under identical conditions, the 5-nitro-1,10-phenanthroline system may be compared with the unsubstituted system in 0.01 M KNO_3 at 15° C; and the 3,4,7,8-tetramethyl-1,10-phenanthroline system may be compared with the unsubstituted system in 0.10 M KNO_3 at 25° C. The values of k compared

are bimolecular rate constants. Values for the 5-nitro-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline systems were calculated assuming a bimolecular path, and the values for the unsubstituted phenanthroline system determined by the radiochemical tracer method are values obtained by extrapolation to infinite concentration. The values reported for the unsubstituted phenanthroline system employing the racemization technique were experimentally determined to be bimolecular. The order obtained by the comparison is 5-nitro-1,10-phenanthroline < 1,10-phenanthroline < 3,4,7,8-tetramethyl-1,10-phenanthroline. This is in order of base strengths and ligand field strengths.

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